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DETERMINATION OF THE INSTABILITY CONSTANTS OF INDIVIDUAL COMPLEXES BY THE METHOD OF DISPLACED EQUILIBRIUM

B. V. Ptitsyn and L. I. Vinogradova

The instability constant seems to be the most important thermodynamic characteristic of complex compounds. Methods for determining it, of which a rather large number are known, may be divided into two groups. To the first group belong methods which are based on a study of the equilibrium of the secondary dissociation of the individual complex, and to the second group belong methods which are based on a study of the process of formation of the complex compound in solution.

A rather complete survey of methods for determining instability constants, and a comparison of their merits was given by K. B. Yatsimirsky [1].

All the methods of the first group are based almost exclusively on the study of the non-displaced dissociation equilibrium of the complex. Their applicability is limited, because only a few methods are known, by which it should be possible, without displacing the equilibrium of the complex, to determine the equilibrium activities of the metal ions and their addends.

It should be pointed out that K. B. Yatsimirsky [1] indicated the possibility of determining the stability of a complex compound by studying the displaced equilibrium of its dissociation, occurring during the process of dissolving the complex compound in the presence of the addend. Strictly speaking, this method is used only for slightly soluble complex compounds.

The methods of the second group have a considerably larger area of applicability, and it is with these, chiefly, that we are concerned at present. However, they give reliable results only in cases where the composition of the complex forming is already known, or may be accurately determined. It is unfortunate that this is not always possible and, as justifiably indicated by K. B. Yatsimirsky [1], special difficulties arise in cases where several complex compounds form in a solution. In view of this, it seems to us that, other conditions being equal, a method based on a study of the equilibrium of dissociation of the individual complex, would always be preferable.

It is known that the process of secondary dissociation of a complex introduces a solvation equilibrium, the constant of which is also called the instability constant. The value of the instability constant found experimentally in a given solvent will, obviously, be the ratio of the instability constant of the given complex and the instability constant of the corresponding solvo-complex. The actual instability constant, characterizing the energies of bonding of the addends to the central atom, will be the equilibrium constant of the dissociation of the complex molecules to the gaseous state.

A. K. Babko [2], and after him, A. A. Grinberg and L. E. Nikolskaya [3], pointed out analogies between the dissociation of weak polybasic acids and complex compounds, as a result of the high field forces existing in the molecules of both types of compounds.

Such analogies, undoubtedly, do exist, but it seems to us that the analogy of the dissociation of weak, polyatomic bases and complex compounds holds to a much greater degree, because their composition and properties are very similar. Analogies between the bases and complex compounds should occasion no surprise, as the OH^- ion does not differ essentially from other negative ions. Actually, by comparing the polarizabilities of OH^- ions and halide ions, we obtain the following:

	F^-	OH^-	Cl^-
polarizability according to Fajans [4]	0.96	1.88	3.57.

According to its electronic structure, the OH^- ion appears to be an analog of the F^- ion [5, 6]. Thus, the tendency of the OH^- ion toward complex formation should be greater than for F^-, and smaller than for Cl^-. The reducing properties of OH^- ion, which, according to A. A. Grinberg [7], are characterized by a tendency toward complex formation, do not contradict this conclusion, because, according to the magnitudes of the oxidation potentials, free hydroxyl occupies a position between fluorine and chlorine, and consequently, the reducing properties of OH^- should be greater than those of F^- and less than those of Cl^-.

The analogy of weak bases and complex compounds is reflected also in the mechanism of their dissociation.

The formation of OH^- ions in solutions of metal hydroxides, which are weak bases, is similar also to the case of solutions containing hydroxyl ions, where the solutions differ from the molecules of weak bases only by the presence of charges, thus accounting for the addition of H^+ ions to the OH^- coordination groups, the bonds of which, in the molecule, approach the covalent.

Strong bases of the MeOH type dissociate in the same way as do halides of the MeX type, because the OH^- and X^- bond in these molecules approaches the ionic, and their crystalline structures are similar. Since any negative group, free or complex-combined, has the capacity to add protons, the dissociation of complex molecules, the addends of which are strong bases, also should proceed by addition of H^+ to the coordinated addend, with subsequent displacement of the water of the addition product.

The foregoing may be illustrated by the following equations:

The dissociation of a weak base proceeds as follows:

$$[Me(OH)_3] + HOH \rightleftharpoons [Me(OH)_2H_2O]^{\cdot} + OH'.$$

The dissociation of the hydroxyl ions proceeds as follows:

$$[Me(OH)_6]''' + HOH \rightleftharpoons [Me(OH)_5H_2O]'' + OH'.$$

The dissociation of the acido-complex ions proceeds as follows:

$$[MeX_6]''' + HOH \rightleftharpoons [MeX_5HX]' + OH',$$

$$[MeX_5HX]'' + H_2O \rightleftharpoons [MeX_5H_2O]'' + HX,$$

$$HX + OH' \rightleftharpoons X' + H_2O.$$

Over all, the following proceeds:

$$[MeX_6]''' + H_2O \rightleftharpoons [MeX_5H_2O]'' + X'.$$

Hydroxy-complexes differ from other acido-complexes only in that the OH^- ion, in comparison with other negative ions, has the greatest affinity for protons, which, together with the low solubilities of the weak bases, is the cause of the lower stability of the hydroxyl ions and of their capacity for being converted to neutral molecules of the base by yielding water. Proceeding from these ideas, we may arrive at the conclusion that the dissociation constants of weak bases are values analogous, formally and by nature, to the instability constants of complex compounds and consequently, the methods for determining both constants also should be analogous.

The instability constants of complex molecules may be determined by studying the interaction of these molecules with ions which produce a displacement of the equilibrium of their secondary dissociations. For example, for complex anions of the $[MeA_6]'''$ type, we can have the equilibrium:

$$[MeA_6]''' + 6H_2O + 6R^{\cdot} \rightleftharpoons [Me(H_2O)_6]^{\cdot\cdot\cdot} + 6RA,$$

where $R^{\cdot}$ is the cation, forming with the addend A either a slightly soluble, or a little-dissociated compound. The second method for determining the instability constant comprises a study of the process of formation of the complex, i.e., a study of the equilibrium:

$$[Me(H_2O)_6]^{\cdot\cdot\cdot} + 6RA \rightleftharpoons [MeA_6]''' + 6H_2O + 6R^{\cdot}.$$

This method has been known a long time and at present has an enormous literature. It is understood that it may be used only when the composition of the complex forming is accurately known. Its theory was developed recently, chiefly by A. K. Babko and I. V. Tananaev.

In essence, the method for determining the instability constant of an individual complex is as follows.

Let us consider the case of the interaction of a complex anion of the $[MeA_6]'''$ type, with an ion forming slightly soluble compounds with its addend, for example, $Ag^{\cdot}$ ion.

If we add $\underline{x}$ g-ions of Ag, where $\underline{x}$ = 1, 2, 3, 4, 5, 6, to a solution of C moles of the complex, the following equilibrium is created:

$$[MeA_6]'' + \underline{x}\ Ag^{\cdot} + \underline{x}\ H_2O \rightleftharpoons [MeA_{6-x}(H_2O)_x]^{x-3} + \underline{x}\ AgA\downarrow$$

$C_{equil.}$ $C'_{equil.}$

The constant for this equilibrium depends on the corresponding instability constant of the complex and on the solubility product of AgA, i.e., the distribution of A^- ions between the complex and the precipitate, depends on the instability constant of the complex and the solubility product of the precipitate.

$$K_{equil.} = \frac{C'_{equil.}}{C_{equil.}\,[Ag^{\cdot}]^x}. \qquad (1)$$

$$K_x^{*} = \frac{C'_{equil.}\,[A']^x}{C_{equil.}}. \qquad (2)$$

Let us substitute $[Ag^{\cdot}]^x = \frac{K^x_{AgA}}{[A']^x}$, where K_{AgA} is the solubility product of AgA.

$$K_{equil.} = \frac{C'_{equil.}\,[A']^x}{C_{equil.}\,K^x_{AgA}} = \frac{K_x}{K^x_{AgA}}; \qquad (3)$$

hence

$$K_x = \frac{C'_{equil.}\,K^x_{AgA}}{C_{equil.}\,[Ag^{\cdot}]^x}.$$

By $C_{equil.}$ and $C'_{equil.}$ we express the initial concentration of the complex C, and we express the equilibrium concentration of the $Ag^{\cdot}$ ions by $[Ag^{\cdot}]$. If we add $\underline{x}C$ g-ions of $Ag^{\cdot}$, then $\underline{x}C - [Ag^{\cdot}]$ g-ions of $Ag^{\cdot}$ enter into reaction; consequently:

$$C'_{equil.} = \frac{xC-[Ag^{\cdot}]}{x} = C - \frac{[Ag^{\cdot}]}{x};\quad C_{equil.} = C - C'_{equil.} = \frac{[Ag^{\cdot}]}{x};\quad K_x = \frac{(xC-[Ag^{\cdot}])\,K^x_{AgA}}{[Ag^{\cdot}]^{x+1}}.$$

When $\underline{x}$ = 1, we obtain an expression for the first instability constant, and when $\underline{x}$ = 2, we obtain an expression for the product of the first and second constants, etc..

For $\underline{x}$ = 6, we obtain an expression for the overall instability constant:

$$K_{overall} = \frac{(xC-[Ag^{\cdot}])\,K^6_{AgA}}{[Ag^{\cdot}]^6}.$$

Repeated use of the second method – study of the solubility of AgA in a solution of the metal salt – led us by analogous reasoning to an identical expression for the overall instability constant.

As early as 1936, A. K. Babko [2] in his work on the mechanism of formation of complex compounds and their stepwise dissociation, calculated the successive instability constants of the oxalate complexes of Al, proceeding from the results of the determination of the solubility of $Ag_2C_2O_4$ in solutions of $Al(NO_3)_3$.

In very considerable number of subsequent works, A. K. Babko, with K. E. Kleiner [8], M. V. Korotun [9], T. N. Richkov [10] and others, significantly developed and proved this method. This method was used by I. V. Tananaev, together with I. B. Mizetskaya and A. D. Vinogradova [11], E. N. Deichman [12, 13] and others, in a series of investigations devoted to studies of the solubility of precipitates in complex (real) analytical systems.

In 1939, I. V. Tananaev [14] proposed the following formula for calculation of the instability constant for the AlF_2^+ ion:

$$K_{AlF_2^+} = \frac{[C_{Al(NO_3)_3} - (Ca^{2+})]\,\frac{L_{CaF_2}}{(Ca^{2+})}}{(Ca^{2+})}.$$

which is entirely analogous to the formula that we presented for the first instability constant:

$$K_1 = \frac{(C-[Ag^{\cdot}])\,K_{AgA}}{[Ag^{\cdot}]^2}.$$

* The $\underline{x}$th instability constant.

As already pointed out, the second method is used only when we know the composition of the complexes forming, and this is certainly not always the case, since during the processes of reaction of the complexes forming, during the dissolving of the AgA precipitate in a solution of the metal salt, as a rule, a whole series of intermediate complex molecules form, so that the calculation of an instability constant, which is necessarily that of a specific complex compound, becomes extremely difficult. The first method is free from these deficiencies, since there we are dealing, not with the step-wise formation of complex compounds of different compositions, but with formation of different products of a step-wise dissociation of a complex compound of a definite composition, i.e., with a definite process which determines the instability constant of the complex compound studied.

It seems to us that a combination of both of these methods may, in a number of cases, lead to very interesting results.

Let us now consider the interaction of a complex compound of the $[MeA_6]^{m}$ type with ions $-$ $H^{\cdot}$ ions to begin with $-$ forming a slightly dissociated compound with the addend.

If, as in the first case, we add $\underline{x}$ g-ions of $H^{\cdot}$, where $\underline{x} = 1, 2, 3, 4, 5, 6$, to a solution of C moles of the complex, then

$$[MeA_6]^{m} + \underline{x}H^{\cdot} + \underline{x}H_2O \rightleftharpoons [MeA_{6-x}(H_2O)_x]^{x-s} + \underline{x}HA.$$

$C_{equil.}$ $C'_{equil.}$

In a similar way, we find that the equilibrium constant for this process is

$$K_{equil.} = \frac{K_x}{K^x_{acid}},$$

where K_x is the $\underline{x}$th instability constant, and $K_{acid.}$ is the acidity constant of the weak acid HA.

Hence

$$K_x = \frac{C'_{equil.}[HA]^x K^x_{acid.}}{C_{equil.}[H^{\cdot}]^x}.$$

Substituting, as in the first case, $C_{equil.}$ and $C'_{equil.}$ by the initial concentration of the complex and the equilibrium concentration of $H^{\cdot}$, and recalling that according to the equation of the reaction, $[HA] = \underline{x}C'_{equil.}$, we obtain in final form

$$K_x = \frac{(xC-[H^{\cdot}])^{x+1} K^x_{acid.}}{[H^{\cdot}]^{x+1}}.$$

For $\underline{x} = 1$, we obtain the expression for the first, and for $\underline{x} = 6$ we obtain the expression for the overall instability constant.

A reverse method, i.e., a study of the interaction of metal ions with molecules of a weak acid, accompanied by liberation of an equal quantity of $H^{\cdot}$ ions, has been repeatedly used in the works of I. V. Tananaev. I. V. Tananaev and E. N. Deichman [12] studied the equilibrium

$$Be^{2+} + HF \rightleftharpoons BeF^{+} + H^{+}.$$

The data obtained were used by the authors for determining the composition of a complex forming in solution.

Proceeding from the pH of the solution measured by the authors, the instability constant for the BeF^{+} ion was calculated as equal to $2.4 \cdot 10^{-5}$. This value agrees practically with the value of the same constant found by I. V. Tananaev and E. N. Deichman [13] for the solubility of PbFCl in $Be(NO_3)_2$ solution, and found to equal $5.1 \cdot 10^{-5}$.

A. K. Babko and K. E. Kleiner [8] studied the equilibrium

$$Fe(SCN)^{2+} + \underline{n}F^{-} \rightleftharpoons FeF_n^{(3-n)} + SCN^{-}.$$

It is obvious from what has been said above that this equilibrium is essentially analogous to the equilibrium arising during the process of complex formation according to the reaction

$$Me^{3+} + HA \rightleftharpoons MeA^{2+} + H^{+},$$

where HA is a molecule of a weak acid.

On the basis of the data obtained, the authors determined the instability constants for the thiocyanate and fluoride complexes of iron.

The resultant equations obviously give the values of the concentration instability constant.

Calculation of the thermodynamic instability constant may be carried out by two methods. In the first, knowing the ionic strengths of the solution and the activity coefficients of the ions participating in the equilibrium, we may determine the activities of these ions directly, and thereby the thermodynamic instability constant. This method, however, is difficult to use, since the activity coefficients of the complex ions are known at the present time in very few cases.

We can determine the concentration instability constants for several solutions having different ionic strengths, construct a graph relating the instability constants to the square roots of the ionic strengths, and extrapolate to an ionic strength equal to zero, to determine the thermodynamic instability constant. In this case, we substitute into the equation, not the thermodynamic value of the solubility product, but the experimentally determined value of the solubility product for a given ionic strength.

The feasibility of determining, by this method, the successive instability constants, corresponding to the different stages of dissociation of the complex particles, will obviously be determined by how much these constants differ from each other. The given case will be governed by the requirement known for polybasic acids, that the two successive constants differ from each other by a factor of 10^3 at least.

It is quite obvious that reactions involving interactions of complex ions either with Ag^+ or H^+ ions may also be studied by potentiometric titration using silver or hydrogen electrodes.

When the successive instability constants are sufficiently different from each other, and their absolute values are sufficiently great, and when the equilibrium in the system is not established too slowly, then on the potentiometric titration curve we may expect the appearance of several rapid changes of potential corresponding to different stages of dissociation of the complex molecules.

Since the metallic hydroxyl-compounds do not differ essentially from other acido-complexes, it follows that the potentiometric titration of polyacid bases by strong acids represents a special case in the study of the equilibrium of a complex molecule with the H^+ ion. The reaction of complex molecules with Ag^+ ions, as was shown, follows the same mechanism as for H^+ ions. It should be pointed out that, from the point of view of the theory of M. I. Usanovich [15], according to which acids seem to be substances giving up cations or adding anions, and bases seem to be substances giving up anions or adding cations, the reaction of a complex molecule with $AgNO_3$ is an acid-base reaction, in which the $AgNO_3$ is, according to M. I. Usanovich, called the acid, and the complex molecule is designated as the base.

When the complex studied is not too stable, and when the addend is a sufficiently strong base, the instability constant may be determined by the simple method of measuring the pH of the solutions, i.e., it is analogous to the method of Bjerrum [16] for the ammoniates and amines.

The proposed method may be used if the following conditions are present. In a determination of instability constant by the equilibrium of a complex ion with Ag^+ ions, it is essential that the solubility of the $Ag_3[MeA_6]$ salt be larger than the solubility of AgA, i.e., that the Ag^+ ions be bound only by A^- ions. In order to study equilibria with H^+ ions, the final acidity constant of the complex acid $H_3[MeA_6]$, should be much larger than the acidity constant of HA, so that the interaction of the H^+ ions with the complex ion $[MeA_6]^{3-}$ may be neglected.

The method described permits the determination of the instability constants of all acido-complex compounds, the addends of which either form difficultly-soluble compounds with various cations, or are strong bases. Under this category may come the complex halides, cyanides, thiocyanides, oxalates, carbonates, chromates, sulfates, borates, acetates, etc., i.e., with few exceptions, it includes almost all of the acido-complexes.

Therefore, it seems to us that, given the necessary conditions, the method of determining the instability constant by the displaced equilibrium of the secondary dissociation of the individual complexes, may acquire a universal character, especially when it is recalled that this method can be used to determine the instability constants of both slightly stable and very stable complexes.

SUMMARY

A method has been proposed for determining the instability constant of an individual complex, based on a study of the displaced equilibrium of its secondary dissociation, during interaction with ions causing the formation of difficultly soluble or slightly dissociated compounds (Ag^+ and H^+ ions). The method is applicable to all acido-complexes, the addends of which give difficultly soluble compounds or are strong bases. The theory of the method has been set forth, and the conditions of its use specified.

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* See Consultants Bureau Translation, page 1015.

** See Consultants Bureau Translation, page 1383.

*** See Consultants Bureau Translation, page 13.

THE HEAT OF FORMATION OF NICKEL CARBONYL

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In spite of the great theoretical and practical interest attributed to the metal carbonyls, their thermochemistry has been extremely little studied. Only a few references in the literature refer to values of the heats of formation of some of the carbonyls, particularly, nickel carbonyl.

Thus, Mittasch [1] showed that the heat of formation of nickel carbonyl at constant pressure amounted to 43.36 kcal per mole. In the same report, Mittasch referred to the investigations of Raikher (1896), from which it followed that the heat of formation of $Ni(CO)_4$ was equal to 59.5 kcal per mole. Thus, the data in the literature are highly divergent.

Ormont [2] in 1946, in reports devoted to the problem of the critical heats of formation of carbonyl compounds, pointed out a series of erroneous conclusions of foreign investigators in the evaluation of the thermodynamic stability of the carbonyls and their derivatives. In this light, it seemed to us important to obtain a clearer picture of carbonyl combustion so as to determine its thermal effect and clarify the degree of uniformity of the thermal effects of carbonyl formation.

In this article we report some of the results of the work carried out for determination of the heats of formation of nickel carbonyl.

EXPERIMENTAL

Method of Combustion of Nickel Carbonyl

In none of the works cited above, where values of the heat of formation of nickel carbonyl were given, were methods of combustion given. Meanwhile, nickel carbonyl has many inherent properties that make it a very difficult object of investigation. It has a very high vapor tension (at 24° C, P = 349 mm [3]), and consequently, a weighed sample of it must be protected from evaporation up to the moment of combustion. Furthermore, nickel carbonyl decomposes on standing; consequently, before combustion the substance must be distilled without decomposition, in order to avoid carrying out the experiment with nickel carbonyl containing finely-dispersed nickel in a suspended condition. The carbonyl ignites spontaneously in oxygen at room temperature, and at elevated pressures the process proceeds explosively. This makes the assembly of a calorimetric apparatus difficult.

In spite of the very active interaction of $Ni(CO)_4$ with oxygen after combustion, we observed an extremely curious phenomenon: on the walls of the small cup in which the nickel carbonyl was placed, a metallic film was observed. It was found to consist of almost 95% pure nickel.

Hence, we came to the conclusion that during the combustion of nickel carbonyl, part of the carbonyl decomposed, because of the heat from the reaction, thus liberating the dense metal. Under these conditions, the usual method of combustion in an open cup did not give reliable results, but led to a number of complications.

Due to the foregoing, we found it expedient to place the carbonyl in a sealed ampoule, in order to avoid loss at weighing and by explosion with the oxygen entering the bomb. In the operation using the ampoule, we also found an inaccuracy, caused by the partial vaporization of the $Ni(CO)_4$ within the bomb, and the participation of not only liquid carbonyl, but also gaseous carbonyl, in the reaction. However, since the error due to the latent heat of vaporization per g of $Ni(CO)_4$ might amount to a total of 40 cal (which is considerably less than the accuracy of the experiment), the elimination of this error was of little practical value. For this or other reasons, and by sealing the carbonyl in an ampoule of 25 ml capacity, we reduced practically to zero the error due to the partial preliminary vaporization of the nickel carbonyl.

Preparation of the weighed sample. A glass ampoule was weighed, filled with an inert gas, and placed in a brass sleeve and cooled by liquid nitrogen. Then into the ampoule we introduced the necessary amount of freshly-distilled nickel carbonyl, which was then cooled and frozen. The ampoule was resoldered and both parts of it were weighed. This made it possible to determine the weight of the carbonyl sealed in the ampoule. The total loss of weight of the glass on resoldering was determined, and amounted to 0.0001 g.

Conditions of combustion. The ampoule was placed in a bomb, and after filling the latter with oxygen, the ampoule was opened.

The explosion of the ampoule brought about a passage of current through the platinum wire (0.3 mm diameter) soldered along the perimeter of the ampoule. Taking into account the large value of the Joule effect in the total heat effect, an accurate measurement of the current strength, voltage, and also a reading of the time of passing of the current through the ampoule, were provided for.

Method of Analysis of the Nickel Carbonyl and Its Combustion Products

The method of analysis was based on the fact that the decomposition of nickel carbonyl by solutions of Br in CCl_4, with formation of $NiBr_2$, proceeds quantitatively in a short time (Dewar and Jones [4]); thus, we have specific conditions for carrying out the analysis.

1. Method of analysis of $Ni(CO)_4$ for nickel content. The weighed sample of nickel carbonyl. Into a conical flask of 250 ml capacity, we poured 30-40ml of carbon tetrachloride, after which the flask was tightly closed and weighed on an analytical balance. Then about 500 mg of freshly distilled nickel carbonyl was poured into the flask. The flask was tightly closed and weighed again. The weight of the carbonyl to be used for the decomposition was determined by difference.

Decomposition of the nickel carbonyl by bromine. The flask containing the carbonyl in CCl_4 was placed on ice. Through the stopper of the tightly closed flask, was inserted a dropping funnel of 100 ml capacity, in which was placed a solution of about 50 ml of bromine in 10 ml of CCl_4. This solution was gradually introduced into the flask.

The carbonyl was decomposed at a rate which was easily regulated by control of temperature and the rate of flow of the bromine solution. The liberated carbon monoxide which might contain carbonyl vapor was exhausted as small bubbles through a separatory funnel, to avoid losses and to permit the carbonyl vapor to react with the bromine solution.

Determination of nickel in the solution after bromination. When decomposition was complete, all the solution of bromine in CCl_4 was dropped into the flask, 100 ml distilled water was added and the total contents heated until the bromine vapor was removed. Simultaneously, the CCl_4 also was vaporized, since the bath temperature was maintained such that continuous, but not vigorous boiling of CCl_4 occurred. The remaining greenish solution was cooled to room temperature, poured into a 200-250 ml volumetric flask and diluted to the mark. Nickel was determined by the Chugaev method.

2. Results of the determination of the nickel in the carbonyl. The results of determining nickel in the carbonyl are presented in Table 1 (the theoretical content of nickel in $Ni(CO)_4$ was equal to 34.38%).

TABLE 1

Expt. No.	Carbonyl taken (g)	Amount of nickel dimethyl glyoxime (g)	Nickel content in the sample (theoretical)	Nickel content in the precipitate obtained	Nickel content found (%)
1	0.5252	0.884	0.1805	0.1795	34.2
		0.882	0.1805	0.1791	34.1
2	0.2956	0.498	0.1016	0.1011	34.2
3	0.8375	1.409	0.2879	0.2861	34.1
4	0.4950	0.833	0.1701	0.1691	34.2
5	0.5188	0.873	0.1783	0.1773	34.1
		0.874	0.1783	0.1775	34.1
				Average	34.1

From the data of Table 1, it is evident that the losses of the carbonyl in work by this method have been reduced, bringing the error of the determination to 0.2%, on the side of somewhat lowered results, for which we can make appropriate corrections.

3. Determination of the nickel content in the combustion products in the calorimetric bomb. The analysis of the reaction products presented difficulties, since we were not certain of the homogeneity of the solid phase. As a rule, this product was of a light-green color with dark disseminations. Analysis showed that the nickel carbonyl

burned to nicklous oxide, with a uniform deposition of metallic nickel, in spite of the presence of oxygen under pressure. The unburned nickel remaining was not less than several per cent, which increased the nickel content in NiO to 81-83% instead of 78.6% (Table 2). The specified composition of the phase made it possible to establish the coefficients x and y, in the equation from which we calculated the heat effect of the reaction; we assumed that total excess of nickel (in contrast to the stoichiometric quantity in NiO) was in the form of β-nickel $[Ni]_\beta$ having a cubic face-centered lattice. This was confirmed by X-ray photographs of the combustion products.

4. X-ray phase analysis of the combustion products. The equation for the reaction of nickel carbonyl with oxygen as usually presented in classical chemistry:

$$Ni(CO)_4\ (l.) + 2\frac{1}{2}O_2 = NiO + 4CO_2 + Q,$$

in reality, cannot be considered as substantial, since, as our experiments showed, first, part of the nickel was deposited in the form of the metal and, second, it is not clear in principle whether the oxide forming has the composition Ni_1O_1; therefore, the equation for the reaction must be written in the following form:

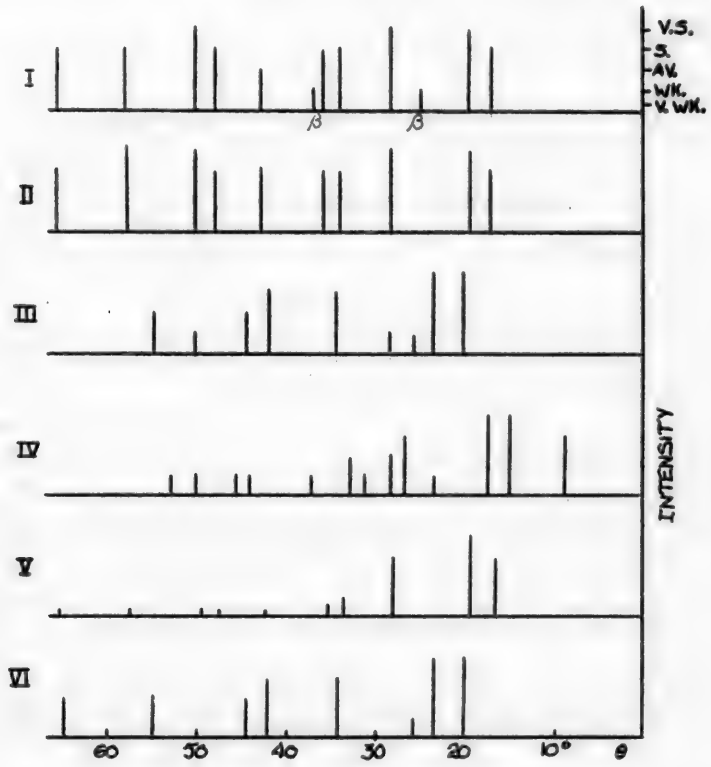
$$Ni(CO)_4\ (l.) + (2 + \frac{xz}{2})\ O_2 = 4CO_2 + xNi_1O_z + (1-x)Ni, \qquad (1)$$

When $z = 1$, the equation assumes the form:

$$Ni(CO)_4\ (l.) + (2 + \frac{x}{2})\ O_2 = 4CO_2 + xNiO + yNi, \qquad (2)$$

where $y = 1-x$.

To determine the composition of the nickel oxide which was made difficult by the presence of metallic nickel in the system, we carried out an X-ray phase analysis of the combustion products.



Results of the X-ray investigation. I) NiO — a yellow powder after combustion (Debye chamber); II) NiO after combustion (asymmetrical method); III) black powder after combustion; IV) chemically pure Ni_2O_3; V) NiO (calculated); VI) 99.95% Ni. Intensity of the lines: v.s. = very strong, s = strong, av. = average, wk = weak, v.wk. = very weak.

The X-ray survey was carried out by the method of Debye. The results are presented on a dash diagram, where the positions and relative intensities of the lines of Ni_2O_3, NiO, β-Ni and the combustion products are shown. From the diagram it is evident that the Ni_2O_3 phase is absent from the combustion products, only the β-Ni phase and the cubic face-centered NiO structure being present. (According to the recent data of Rooksby [5], this phase actually has a small rhombohedral anorthogonality which does not affect its identification.) In order to account for possible fluctuations in the combustion of the NiO phase (this problem was incapable of definite solution by chemical analysis because of the two-phase nature of the system and the presence in it of metallic nickel), we set up an investigation by the method of reversion X-ray exposure in a modified Sachs chamber.

On the other hand, the solid combustion product of NiO was heated in a "Mars" furnace in a current of O_2 at 1100° C, and after calcination it was again studied by the method of reversion X-ray exposure. No displacement of the lines was observed; here it was possible to conclude that, in the combustion products in the bomb, the O:Ni ratio, apparently, was very close to unity. This permitted us to accept equation (2), as a first approximation to the equation of the reaction. Then, considering the data from the chemical analysis, it was not difficult to determine the values of x and y in equation (2), and to calculate the heat of formation of nickel carbonyl.

Procedure of Combustion and the Calculation of the Heat Effects

1. Determination of thermal capacity of the calorimeter. The thermal capacity of the calorimeter, with the Kroker-Maller bomb, was determined with benzoic acid having a heat of combustion of 6311 cal/g, which was burned in the form of tablets having cotton threads pressed into them. The thread was tied to an iron wire, which was fastened between the contacts of the bomb.

For the heat of combustion of the iron wire and the cotton thread, the tabulated values of the heats of combustion were used. The initial and final periods lasted 10 minutes, and the main period was 6-7 minutes.

We made 7 combustions, on the basis of which we established the average magnitude of the thermal capacity of the calorimeter as equal to 2372 ± 6 cal.

Correction for the heat exchange of the calorimeter was introduced according to the formula of Regnault-Pfaundler-Usov [6].

TABLE 2

Number	Characteristic	Experiment		
		1	2	3
1	Weight of carbonyl (in g)	4.5016	4.4239	4.1755
2	Heat value of the calorimeter (in cal)	2372	2372	2372
3	Increase of temperature	3.53	3.142	2.82
4	Total quantity of heat (in cal) for the sample Q'	8317	7403	6644
5	Time of passage of current (in sec.)	330	160	5
6	Amount of heat from passage of current (in cal)	1078	555	81
7	Amount of heat obtained from combustion of the carbonyl (in cal per sample)	7295	6897.63	6608.4
8	Heat of combustion of the carbonyl (in cal per 1 g)	1620	1561	1583_3
9	Heat of combustion of the carbonyl (in kcal per mole of $Q_{1, 2, 3}$)	276_5	266_4	269_3
10	Average percent content of nickel in the combustion products	81.3	83.9	82.1
11	Content of O_2 in Ni + NiO (in %)	18.7	16.1	17.9
12	Percent of Ni bound to oxygen in NiO	68.6	59.1	65.6
13	Percent of free nickel	12.7	24.8	16.5
14	Coefficient for Ni(y)	0.155	0.295	0.251
15	Coefficient for NiO(x)*	0.845	0.705	0.749
16	Heat of formation of $Ni(CO)_4$ from Ni + 4CO in kcal (Q_v**)	43.8	45.6	45.3

* Average value is 0.766.

** Average value of 44.9 ± 1 kcal.

Moreover, we made a correction to the increase of temperature in the experiment, taking into account the projection of the column of mercury according to the rating of the Beckmann thermometer used, and we also made a correction for the Joule effect produced by the passage of current through the platinum wire soldered into the

ampoule.. For this, we stabilized the voltage of the circuit and measured the current strength, the time, and the voltage on the clamp of the bomb at the moment when the ampoule was exploded. The results of the combustion of the Ni-carbonyl are presented in Table 2.

No correction was made for the variation in $\left(\frac{\partial \Delta E}{\partial p}\right)_T$ with transition from 30 to 1 atm, since calculation on the basis of data from Rossini and Frandsen [7] led to values that were smaller than the experimental error.

As shown by the results of the chemical and X-ray phase analyses, although during the combustion the same phases, NiO and Ni, were produced, their proportions in each of these individual experiments varied to some extent; therefore, the heat of combustion per 1 g and per 1 mole of the carbonyl also varied. This circumstance required that we calculate the heat of formation of the carbonyl for each experiment individually without using the average heat of combustion.

Using the data of Table 2 it was possible to write for all three of the samples in that table, the equation of the reaction, by which, for all practical purposes, the combustion of nickel carbonyl took place.

The corresponding equations have the form:

1) $Ni(CO)_4 + \left(2 + \frac{0.845}{2}\right) O_2 = 0.845\ [NiO] + 0.155\ [Ni] + 4CO_2 + 276_5$ kcal.

2) $Ni(CO)_4 + \left(2 + \frac{0.705}{2}\right) O_2 = 0.705\ [NiO] + 0.295\ [Ni] + 4CO_2 + 266_4$ kcal.

3) $Ni(CO)_4 + \left(2 + \frac{0.749}{2}\right) O_2 = 0.749\ [NiO] + 0.251\ [Ni] + 4CO_2 + 269_3$ kcal.

On the basis of these equations it is not difficult to calculate the heat of formation of nickel carbonyl according to the equation:

$$[Ni]_\beta + 4CO = Ni(CO)_4\ (l.) + Q_{1,\ 298};$$

substituting for Q_1, Q_2 and Q_3 in the foregoing reaction equations, the data determined during combustion.

Hence we obtain:

1) $\Delta' E_{298}\ Ni(CO)_4 = 0.845 \cdot 58.9 + 270.5 - 276_5 = -43.77$ kcal/mole.

2) $\Delta'' E_{298}\ Ni(CO)_4 = 0.705 \cdot 58.9 + 270.5 - 266_4 = -45.62$ kcal/mole.

3) $\Delta''' E_{298}\ Ni(CO)_4 = 0.749 \cdot 58.9 + 270.5 - 269_3 = -45.32$ kcal/mole.

The average of the three determinations is equal to

$$-\frac{43.8 + 45.6 + 45.3}{3} = -44.9 \pm 1 \text{ kcal/mole}$$

The standard enthalpy of the reaction $[Ni]_\beta + 4(CO) = Ni(CO)_4\ (l.)$ is equal to:

$$\Delta H^0_{f,\ 298} = \Delta E^0_{298} - 4RT = -44.9 - 2.4 = -47.3 \pm 1 \text{ kcal/mole.}$$

The accuracy of the determination of the heats of formation of nickel carbonyl from Ni and CO is governed to a great extent by the accuracy with which the fractional coefficients in the equation of the combustion reaction, characterizing the number of components and the reaction products, are established. This situation is all the more significant, since small fluctuations of the composition of the nickel oxides may occur with a corresponding change in the thermal effects of their formation.

SUMMARY

On the basis of the investigation that we carried out, the heat of formation of nickel carbonyl was determined. The variations of the latter depended on the fluctuations of the composition of the nickel oxide forming. The accuracy of these determinations was estimated to be ± 2%.

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DOUBLE DECOMPOSITION IN A RECIPROCAL SYSTEM OF THE SULFATES AND TUNGSTATES OF LITHIUM AND LEAD

I. N. Belyaev

In a ternary reciprocal system with the participation only of cations having outer electron shells of the inert gas type, the irreversibility increases in a series from lithium to cesium, if some divalent cation, for example, be in combination with the alkali metals. Thus, in the series M, Ca ‖ F, Cl (M = Li, Na, K, Rb, Cs) the most reversible the system Li, Ca ‖ F, Cl, the most irreversible the system Cs, Ca F, Cl (stratification [1]). In this series of reciprocal systems, such an order is altered and the "conditionally" calculated heat effects of the reactions are interchanged. Thus, for the system Li, Ca‖F, Cl they are at a maximum, but for the system Cs, Ca‖F, Cl they are at a minimum.

For many systems involving the participation of cations having 18 or 18 + 2 electrons in their shells, the "conditional" heat effects of the reactions (calculated at 25°) do not offer the possibility of judging the direction of the exchange reactions. Calculations of the polarities of the halides of Ag, Cd, Pb, and Tl show that, for systems involving the participation of these cations, the character of the changes in the series from Li to Cs must be the reverse of that for systems involving the participation of cations having electron shells of the inert gas type, i.e., the irreversibility must increase in the series from Cs to Li. It is unfortunate that, for the sulfates and tungstates, it has as yet not been possible to calculate the polarities, and it is impossible to judge the nature of the changes of the systems in the series Cs → Li by the differences of the polarities for a combination of the cations of the series Cs → Li with cations having an outer electron layer of 18 or 18 + 2 electrons.

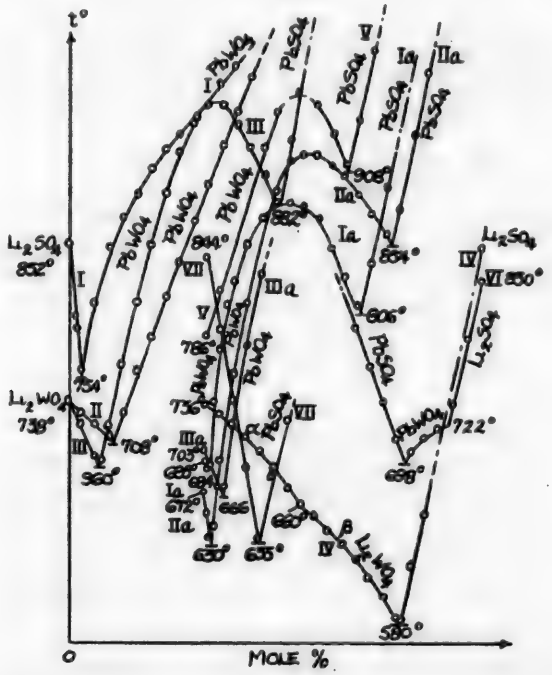

Fig. 1. Fusion system. I) Diagonal section, Li_2SO_4; II) binary system, Li_2WO_4–$PbWO_4$; III) diagonal section, Li_2WO_4–$PbSO_4$. Curves Ia, IIa and IIIa refer to sections I, II and III of Table 2; the remaining numbers on the curves agree with the numbers of the sections in Table 2.

In the present report, we present the results of an investigation, by visual-polythermal methods, of the crystallization surfaces of a system of sulfates and tungstates of lithium and lead, the final members of the series Li(Na, K)Pb‖SO_4, WO_4.

EXPERIMENTAL*

The production of the salts, $PbWO_4$ and $PbSO_4$, was described earlier [3, 4]. Chemically pure lithium sulfate was recrystallized (m.p. 852°); lithium tungstate was prepared by fusion of lithium carbonate (pure for analysis) with tungstic anhydride (m.p. 788°).

Binary systems: The system lithium tungstate–lead tungstate (Table 1, Fig. 1), studied for the first time, has a eutectic point at 16.5%** lead tungstate and 708°. The systems lithium tungstate–lithium sulfate, lithium sulfate–lead sulfate, and lead sulfate–lead tungstate were studied earlier [4, 5]. The first two are simple eutectic systems, with the eutectics: for the first, at 593° and 68% lithium sulfate, and for the second, at 632° and 22% lead sulfate. We repeated the investigation of both systems, and the data obtained did not disagree with the previous data, within the limits of experimental error. The system lead tungstate–lead sulfate was characterized by the presence of a limited solubility in the solid state with a eutectic point at 995° and 50% lead tungstate.

* V. Miroshnikov assisted in the experimental portion of this work.

** The percentage here was molecular.

TABLE 1

(1) Added component; (2) mole % of added component; (3) temperature of appearance of the first crystals)

1	2	3	1	2	3	1	2	3
$LiWO_4-PbWO_4$			diagonal section of $Li_2SO_4-PbWO_4$			diagonal section of $Li_2SO_4-PbSO_4$		
$PbWO_4$	0	738	$PbWO_4$	0	852	$PbSO_4$	0	738
	5	729		3	791		5	720
	10	720		4	774		10	698
	15	710		5	760		12.5	696
	20	729		7.5	778		15	720
	25	760		10	810		17.5	743
	30	786		15	852		20	765
	35	816		20	873		25	810
	40	841		25	890		30	852
	45	871		30	909		35	891
	50	891		35	924		40	920
	55	925		40	935		45	943
	60	950		45	946		50	956
	65	975		50	956		55	954
				55	970		60	940
				60	983		65	924
				65	955		70	906
							75	883
							80	930
							82.5	964

TABLE 2

A) $LiWO_4$, B) Li_2SO_4, C) $PbWO_4$, D) $PbSO_4$

Section	Composition of original mixture	M.p. of original mixture	Added component	Intersection of the crystallization branches						
				branch	intersection of 1 & 2		branch	intersection of 2 & 3		branch
				1	% D	t°	2	% D	t°	3
I	20% A 80% B	695°	D	B	2.5	684	C	56.0	806	D
II	50% A 50% B	672	D	A	2.5	630	C	67.0	854	D
III	80% A 20% B	703	D	A	7.0	666	C			
IV	2.5% C 97.5% A	736	B	A	36.0	660	C-A	70.0	580	B
V	30% C 70% A	786	D	C	71.0	908	D			
VI	2.5% A 97.5% B	830	D	B	11.0	722	C	27.0	698	D
VII	1% A 99% C	844	D	B	20.0	635	D			

The diagonal section of lithium sulfate–lead tungstate (Table 1, Fig. 1) has the form of the usual binary systems and has a eutectic point at 754° and 5.5% lead tungstate, and therefore, is a stable diagonal section of the reciprocal system studied.

The diagonal section of the system, lithium tungstate–lead sulfate (Table 1, Fig. 1) was metastable, and had three branches of crystallization intersecting at 690 and 882° and a 12 and 76% lead sulfate, respectively.

In order to calculate the relief of the crystallization surfaces of all the systems, we studied 7 internal sections. The results are presented in Table 2 and Fig. 1.

From Fig. 2, in which is represented a projection of the three-dimensional diagram of the reciprocal system onto the composition rectangle, it is evident that the system studied is irreversibly reciprocal, with a stable diagonal section of lead tungstate–lithium sulfate. The distribution of the isotherms shows that the systems approach simple systems.

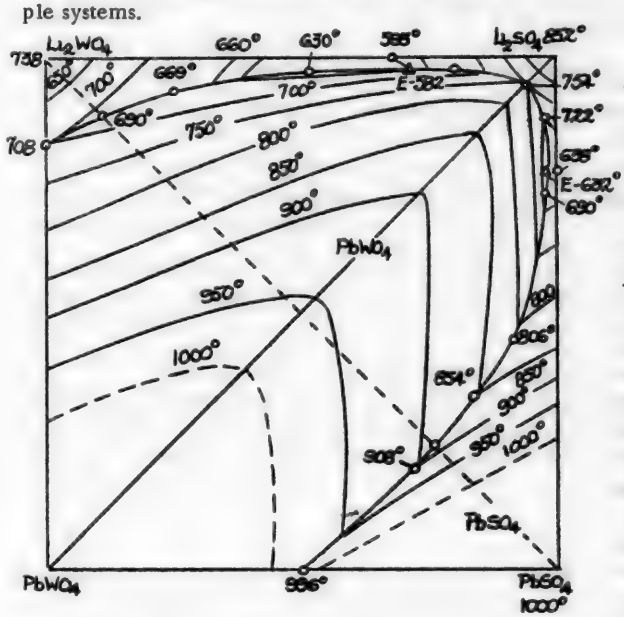

Fig. 2. Projection of the liquidus area of the system Li, Pb‖SO_4, WO_4 on the basis of a square.

Comparison of Fig. 2 with the reciprocal systems of the sulfates of sodium and lead [2], and the sulfates of potassium and lead [3], shows that in the series Li(Na, K), Pb‖SO_4, WO_4 the irreversibility increases from potassium to lithium. The system K, Pb‖SO_4, WO_4 is a transition from the diagonal to the non-diagonal, and has three almost "equally valid" •sections, having the characteriof the binary systems ($K_2SO_4 \cdot 2PbSO_4$ – $-PbWO_4$; $K_2WO_4 \cdot PbWO_4 - K_2SO_4$ and $K_2SO_4 - PbWO_4$). The system Na, Pb‖SO_4, WO_4 is irreversible-reciprocal with the stable section $Na_2SO_4 - PbWO_4$, but the intersection of the isotherms at the $PbWO_4$ peak is smoother than in the system Li, Pb‖SO_4, WO_4. An analogous character of the change of the reciprocal systems should be expected also in the series Li, (Na, K) Pb‖SO_4, MoO_4, since the systems Na, Pb‖SO_4, MoO_4 [6] and K, Pb‖SO_4, MoO_4 [7] are entirely analogous to systems involving the participation of WO_4. Thus, it is possible to consider as established the fact that, for a combination of the sulfates and tungstates (molybdates) of lead with the sulfates and tungstates (molybdates) of the alkali metals, the irreversibility of the double decomposition reaction increases in the series from potassium to lithium, while the combination of an alkali metal with some divalent cation having an outer shell of the inert gas type takes place reversibly, the irreversibility increasing in the series from lithium to potassium.

In all the systems considered involving the participation of lead the equilibrium in the melts was displaced toward the side of combination of cations having 18 + 2 electrons in their shell with anions containing an element having an incomplete d-electron layer. This confirms the assumption formulated earlier [8], that for the double decomposition of salts containing 1 cation having 18 or 18 + 2 electrons in their shells and 1 anion, having in its composition an element having an incomplete d-electron layer, the equilibrium will always be displaced toward the side of the combination of the cation having 18 or 18 + 2 outer shell electrons with the anion containing an element having an incomplete d-electron shell.

SUMMARY

1. The crystallization surfaces of ternary reciprocal systems of the sulfates and tungstates of lithium and lead were studied by the visual-polythermal method. The systems belong to the irreversible-reciprocal systems and approach simple systems. The lithium sulfate–lead tungstate diagonal is stable.

2. It was shown that, for a series of reciprocal systems of the sulfates and tungstates (molybdates) of lead and the alkali metals, the irreversibility of the double decomposition reaction in melts increases in the series from potassium to lithium.

3. We confirmed our previously advanced hypothesis that double decomposition reactions in melts involving participation of cations having 18 or 18 + 2 shell electrons and anions containing an element having an incomplete d-electron shell, are always directed toward the side of combinations of the latter.

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* See Consultants Bureau Tmaslation, page 1789.
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SOLUBILITY IN THE SYSTEM $CaCO_3$–$MgCO_3$–H_2O AT DIFFERENT TEMPERATURES AND PRESSURES OF CO_2

O. K. Yanatyeva

The problem of determining the action of water on dolomite has been the subject of study of a number of investigators [1-4]; however, until now the problem remained unsolved, and the opinions of different authors on the problem were inconsistent.

The present report gives the results of investigations of the solubility of dolomite ($CaCO_3 \cdot MgCO_3$) in pure water, and also in presence of its components – calcite ($CaCO_3$) and magnesite ($MgCO_3$) – under polythermal and polybaric conditions.

The preparations used for the investigation were of native purity: Shishimsk dolomite was obtained from the Laboratory of Decorative Stone of the Academy of Architecture of the USSR, and contained 0.27% insoluble matter, 0.40% $Fe_2O_3 + Al_2O_3$, 53.74% $CaCO_3$, 45.46% $MgCO_3$, and was free of admixtures calcite and magnesite; the white Satkinsk magnesite and transparent calcite (Iceland spar) were from the mineralogical museum of the Academy of Sciences of the USSR.

TABLE

Solubility in the System $CaCO_3$–$MgCO_3$–H_2O

Point No.	Temperature	Millimoles per 1000 g of solution		pH of solution	Solid phase
		$Ca(HCO_3)_2$	$Mg(HCO_3)_2$		
		At $P_{CO_2} \sim 1$ atm			
1	0°	15.08	–	–	Calcite
2		13.64	1.32	–	Calcite + dolomite
3		5.34	5.40	–	Dolomite
4		3.40	12.27	–	Dolomite + magnesite
5		–	22.52	–	Magnesite
6	25°	8.98	–	–	Calcite
7		8.10	1.18	5.8	Calcite + dolomite
8		3.21	3.28	5.7	Dolomite
9		2.50	11.26	6.0	Dolomite + magnesite
10		–	16.50	–	Magnesite
11	55°	6.09	–	–	Calcite
12		4.23	2.17	6.69	Calcite + dolomite
13		3.00	3.08	–	Dolomite
14		2.15	7.39	6.92	Dolomite + magnesite
15		–	15.59	–	Magnesite
16	70°	3.45	–	7.66	Calcite
17		2.03	2.55	7.82	Dolomite + calcite
18		1.55	5.89	7.84	Dolomite + magnesite
		At $P_{CO_2} \sim 0.0012$ atm			
19	25°	0.81	–	–	Calcite
20		0.39	0.94	7.76	Calcite + dolomite
21		0.40	1.02	7.78	Dolomite + calcite
22		0.32	1.20	7.87	Dolomite + magnesite
23		–	1.65	–	Magnesite

Note: For point No. 17, the data are for pure dolomite and for its mixture with calcite at 70°. For point No. 20, we used a mixture of dolomite with calcite. For point No. 21, pure dolomite was used.

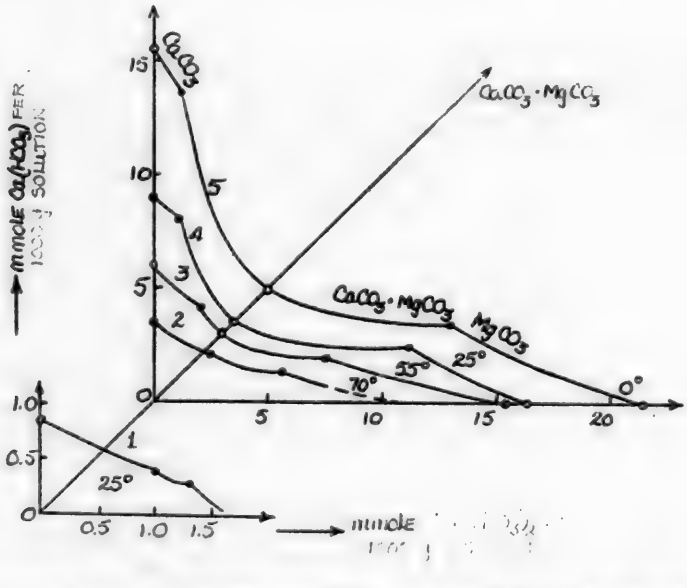
The solubilities were studied at temperatures of 0, 25, 55 and 70° and at CO_2 partial pressures of about 1 and 0.0012 atm. The 0° temperature was maintained in a large Dewar vessel (8 liters) filled with ice; temperatures of 25, 55 and 70° were maintained in a water thermostat using a mercury-toluene thermoregulator; the laboratory air served as the source of the low partial pressure CO_2, the air being blown through the mixture in the vessel by means of a water-jet pump.

A more detailed characterization of the preparations, a description of the apparatus and the method of investigation are presented in a report published earlier [5].

The data obtained on the solubilities in the system $CaCO_3-MgCO_3-H_2O$ are expressed in millimoles of salt per 1000 g of solution, and are presented in the Table and in the form of an equilibrium diagram in the Figure.

It is obvious from the diagram that the general forms of all the solubility isotherms of the system are alike, since each of them consists of three branches corresponding to the crystallization of calcite, dolomite and magnesite; however, the crystallization branch for calcite invariably increases with an increase of temperature or with a decrease of the CO_2 content in solution, but the dolomite branch, on the other hand, decreases and the region of its existence in the polytherm gradually plays out.

The sharp change of the solubility of calcite with temperature is indicated by the character of the solubility of the double compound – dolomite. From the Table it is obvious that solutions, saturated with pure dolomite, at 0, 25 and 55° and at a P_{CO_2} equal to about 1 atm contain equal numbers of millimoles of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, i.e., dolomite dissolves without decomposition. At 70° the ratio of the salts in the solution changes, with $Mg(HCO_3)_2$ predominating, and at the bottom of the vessel calcite appears as the additional solid phase (together with dolomite), forming because of the decomposition of the dolomite. An analogous picture is observed also for $P_{CO_2} \sim$ 0.0012 atm at 25°.



Equilibrium diagram of the system $CaCO_3-MgCO_3-H_2O$. 1) ~ 0.0012 atm P_{CO_2}; 2, 3, 4, 5) ~ 1 atm P_{CO_2}.

The change of the congruent solubility of dolomite with an increase of temperature and a decrease of the partial pressure of CO_2 is reflected graphically on the equilibrium diagram of the system $CaCO_3-MgCO_3-H_2O$, where a straight line connecting the composition point of dolomite with the origin of the coordinates intersects the crystallization branches of dolomite on the 0, 25 and 55° isotherms (with congruent solubility), and intersects the calcite branch (with congruent solubility) on the 70° isotherm and the 0.0012 atm isobar.

Results of the measurement of the pH of the individual solutions of the system* are extremely interesting, the congruent solubility being observed at low pH values of the solution (below 7), and the incongruent at elevated values (above 7) (see the Table).

* The measurements were made by V. N. Sveshnikov, to whom we express our thanks.

Thus, the results of the systematic investigation of the solubility of dolomite show the variable character of the solubilities, depending on the conditions (pH, P_{CO_2}, temperature, etc.) and impart complete clarity to the problem discussed.

The solution of this problem, having at first glance a purely theoretical character, at the same time is of important practical value: the data obtained direct utilization of the carbonate rocks (dolomites, dolomitized limestones, etc.) in the proper regions in hydrotechnical construction, and also are useful for clarifying the conditions of formation and the stability of the dolomites in nature.

SUMMARY

1. The solubilities in the system $CaCO_3-MgCO_3-H_2O$ were studied at 0, 25, 55 and 70° and at a P_{CO_2} of about 1 to 0.0012 atm.

2. The data obtained showed the relationship of the character of the solubility of dolomite in the system to the pH of the medium, to P_{CO_2} and to the temperature; at pH values of less than 7 we observed the solubility of dolomite without decomposition; at pH values above 7, and also at low P_{CO_2}, we observed its solubility with decomposition.

3. Proceeding from the structure of the equilibrium diagram of the system

$$CaCO_3-MgCO_3-H_2O$$

at lower P_{CO_2} (below 0.0012 atm) we should expect disappearance of the dolomite area in the system, i.e., complete decomposition of the dolomite by the action of water.

4. The results of the investigation are of value for clarifying the conditions of formation and stability of dolomite in nature, and also for their utilization in hydrotechnical construction.

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REACTIONS IN MELTS OF THE NITRATES AND NITRITES OF THE METALS IN THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM

XVI. INVESTIGATION OF TERNARY SYSTEMS OF THE NITRATES OF CESIUM, THALLIUM AND CADMIUM

P. I. Protsenko and V. V. Rubleva

A pecularity of some of the nitrates of the metals of the first and second groups of the D. I. Mendeleev periodic system in melts seems to be their clearly expressed tendency toward vitrification. As a rule, this phenomenon, which is usually observed on cooling the melt, is accompanied by supercooling, increase of viscosity, and usually complex formation. From this point of view, the ternary systems of the nitrates of cesium, thallium and cadmium are of special interest. The investigation of this system, like the preceding, was carried out by the visual-polythermal method of physico-chemical analysis.

Binary Systems

For the first time, we studied the binary system cesium nitrate—thallium nitrate. The components of this system form a continuous series of solid solutions, for which the lowest melting point on the liquidus curve corresponds to the melting point of pure thallium nitrate (Fig. 1).

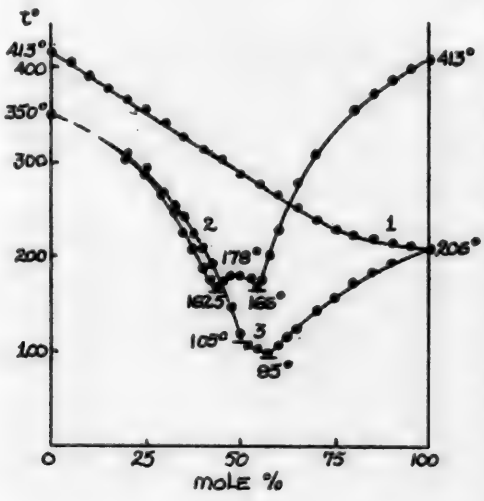

Fig. 1. Binary systems. 1) $CsNO_3$—$TlNO_3$, 2) $Cd(NO_3)_2$—$(CsNO_3)_2$; 3) $Cd(NO_3)_2$—$(TlNO_3)_2$.

The melts of the salt mixtures of this system, at all concentrations, were clear, and crystallized readily.

We also investigated the binary system, cadmium nitrate—thallium nitrate for the first time. The fusion diagram of the system has three branches of crystallization: cadmium nitrate, the chemical compound $Cd(NO_3)_2 \cdot 2TlNO_3$, and thallium nitrate. On heating above 300°, we observed the decomposition of the melts with the liberation of nitrogen peroxide and formation of the dark cinnamon-colored precipitate of cadmium oxide; therefore, the cadmium nitrate branch of crystallization was studied from an ordinate composition of 20% thallium nitrate. In the concentration interval from 45 to 60% thallium nitrate, the viscosity of the melt increased appreciably, and vitrification took place. The eutectic point was found experimentally and was verified graphically; it corresponded to 57% thallium nitrate and m.p. of 95°. The transition point on the fusion curve corresponds to a m.p. of 105° (Fig. 1). The melts corresponding to the remaining parts of the composition diagram, were clear and crystallized readily. The composition of the compound, melting with decomposition, may be expressed by the formula $Cd(NO_3)_2 \cdot 2TlNO_3$.

The binary system, cadmium nitrate—cesium nitrate, according to the literature had not been investigated. The composition diagram of this system also consists of three crystallization branches: cadmium nitrate, the chemical compound $Cd(NO_3)_2 \cdot 2CsNO_3$, the maximum of which on the liquidus curve corresponds to a temperature of 178°, and cesium nitrate. Investigation of this system was carried out from the ordinate of 20% cesium nitrate. At smaller contents, the melt decomposed with liberation of nitrogen peroxide. The eutectic mixture containing 43.5% of cesium nitrate, melted at 162.5°, and the mixture containing 54.5% cesium nitrate melted at 166°. The eutectic point was found experimentally and verified by the intersection of the liquidus curves. At concentrations from 40 to 60%* cesium nitrate, the melt crystallized poorly, being readily supercooled and converted to a vitreous mass.

* The compositions of the components here are given as equimolecular percentages.

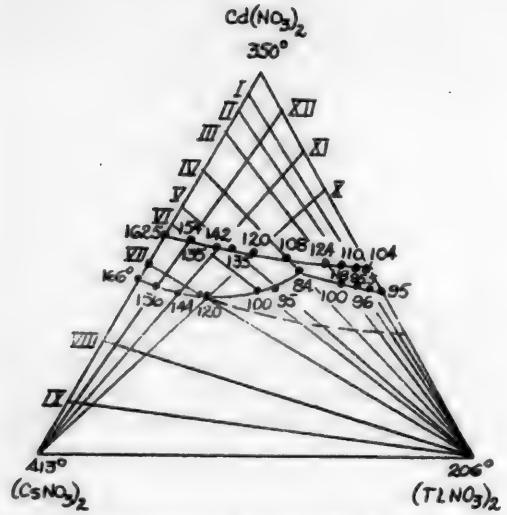

Fig. 2. Arrangement of the sections in the ternary system.

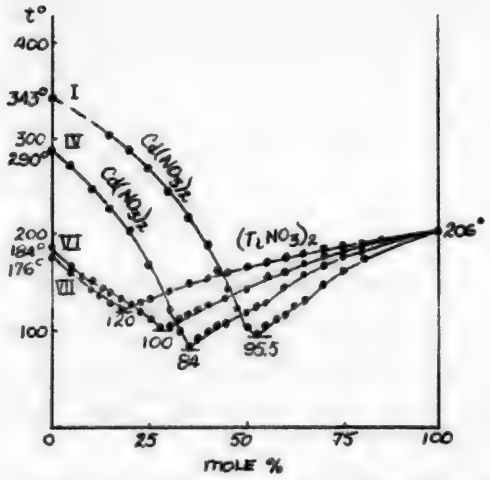

Fig. 3. Sections in the ternary system. I) 5% $(CsNO_3)_2$ + 95% $Cd(NO_3)_2$ → $(TlNO_3)_2$; IV) 25% $(CsNO_3)_2$ + 75% $Cd(NO_3)_2$ → $(TlNO_3)_2$; VI) 40% $(CsNO_3)_2$ + 60% $Cd(NO_3)_2$ → $(TlNO_3)_2$; VII) 50% $(CsNO_3)_2$ + 50% $Cd(NO_3)_2$ → $(TlNO_3)_2$.

Ternary Systems

In order to elucidate the nature of the interactions occurring in melts of the nitrates of cadmium, thallium and cesium in a ternary system, we investigated 12 sections; the arrangement and form of the liquidus curves are shown in Figs. 3, 4, and 5, and the composition transition points, and the melting points of the mixtures of components corresponding to these points, are presented in the Table.

In Fig. 6 an orthogonal projection of the course of crystallization onto a cesium nitrate–thallium nitrate triangle is shown.

The experimental data for all the ternary systems are generalized in the projection of the three-dimensional isotherm composition diagram (Fig. 7).

As should be expected, proceeding from the type of binary system which constitutes the sides of the triangle the ternary system of the nitrates of cadmium, cesium and thallium has four areas of crystallization: cadmium nitrate, an isomorphic mixture of cesium and thallium nitrates, the chemical compound $Cd(NO_3)_2 \cdot 2CsNO_3$ and the chemical compound $Cd(NO_3)_2 \cdot 2TlNO_3$.

The formation in the binary system cadmium nitrate–thallium nitrate, of the compound $Cd(NO_3)_2 \cdot 2TlNO_3$ was confirmed also for the ternary system. The small area of crystallization of this compound (about 2%) indicates its low stability.

The formation in the binary system cadmium nitrate–cesium nitrate, of the chemical compound $Cd(NO_3)_2 \cdot 2CsNO_3$ melting without decomposition, also is verified by the presence of the corresponding area of crystallization in the ternary system, corresponding to 7.35% of the total area of the triangle.

We should call attention to the fact that on the cadmium nitrate–thallium nitrate side of the triangle, and on the curves of sections III, IV and VI, there are small discontinuities, obtained in all cases at the same temperature of 130°. We must assume that they correspond to the conversion of the α-modification of thallium nitrate to the β-modification. The area of crystallization of the designated modifications of thallium nitrate is shown by dotted lines (Fig. 7).

Investigation of the above-mentioned ternary systems was accompanied by great difficulties, arising from the sharply expressed tendencies of the melts toward supercooling, increased viscosities and vitrification. These difficulties were overcome by energetically rubbing the walls of the vessel with the stirrer, employing long periods of holding the melt at a temperature close to the crystallization point, and introduction of seeds from previously crystallized melts. The correspondence of the temperature of the appearance of the first, and temperature of disappearance of the last crystals, in such cases, was within 2-3°.

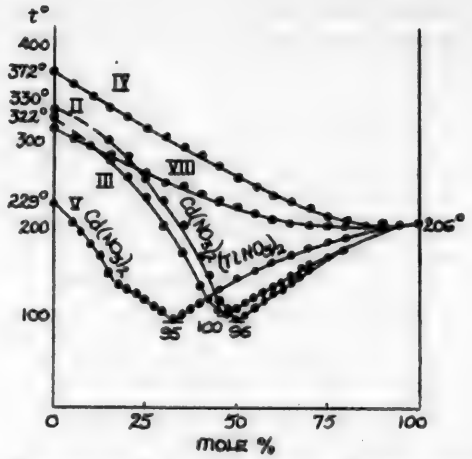

Fig. 4. Sections in the ternary systems. II) 10% $(CsNO_3)_2$ + 90% $Cd(NO_3)_2$ → $(TlNO_3)_2$; III) 15% $(CsNO_3)_2$ + 75% $Cd(NO_3)_2$ → $(TlNO_3)_2$; V) 35% $(CsNO_3)_2$ + 65% $Cd(NO_3)_2$ → $(TlNO_3)_2$; VIII) 70% $(CsNO_3)_2$ + 30% $Cd(NO_3)_2$ → $(TlNO_3)_2$; IX) 85% $(CsNO_3)_2$ + 15% $Cd(NO_3)_2$ → $(TlNO_3)_2$.

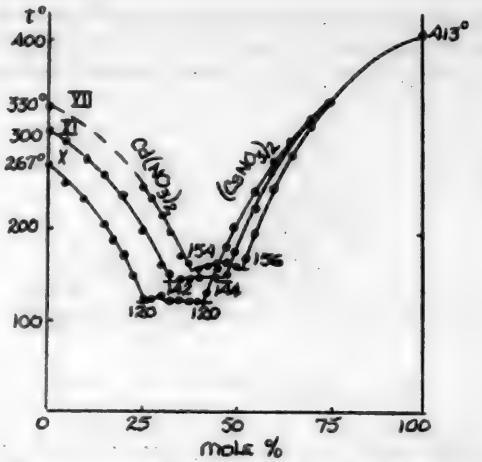

Fig. 5. Sections in the ternary systems.. X) 30% $(TlNO_3)_2$ + 70% $Cd(NO_3)_2$ → $(CsNO_3)_2$; XI) 20% $(TlNO_3)_2$ + 80% $Cd(NO_3)_2$ → $(CsNO_3)_2$; XII) 10% $(TlNO_3)_2$ + 90% $Cd(NO_3)_2$ → $(CsNO_3)_2$.

TABLE

Section No.		Equimolecular percents			M.p. of the composition of the transition point
		$TlNO_3$	$CsNO_3$	$Cd(NO_3)_2$	
I	a*	48.5	3	48.5	110
	b**	44.9	2.6	52.5	95.5
II	a	49.3	5.7	45.0	118.0
	b	44.9	5.1	50.0	96.0
III	a	50.0	9.0	41.0	124.0
	b	44.5	8.1	47.5	100.0
IV	a	51.8	17.2	31.0	108.0
	b	48.4	16.1	35.5	84.0
V	a	53.5	29.0	17.5	135.0
	b	43.9	23.6	32.5	95.0
VI	a	55.5	37.0	7.5	155.0
	b	42.9	28.6	28.5	100.0
VII	a b	41.0	41.0	18.0	120.0
VIII***		17.0	6.0	14.0	80.0
IX***		0.5	4.5	95.0	204.0
X	a	52.2	25.0	22.8	120.0
	b	41.0	41.0	18.0	120.0
XI	a	54.2	32.0	13.0	142.0
	b	42.0	47.0	11.0	144.0
XII	a	55.5	38.0	6.5	154.0
	b	43.6	51.0	5.4	156.0

* Composition of the first transition point

** Composition of the second transition point.

*** Minimum.

The recording by A. P. Rostkovsky [1] of the phenomenon of vitrification, which he observed during a study of the binary system of calcium and potassium nitrates, was not only confirmed by us in the same system, but was also observed in a more clearly expressed form in an entire series of binary and ternary nitrate systems; thus, it is extremely noteworthy! that, both in this investigation and in earlier work on the system [2-5], vitrification occurred only within definite concentration limits of the nitrates reacting.

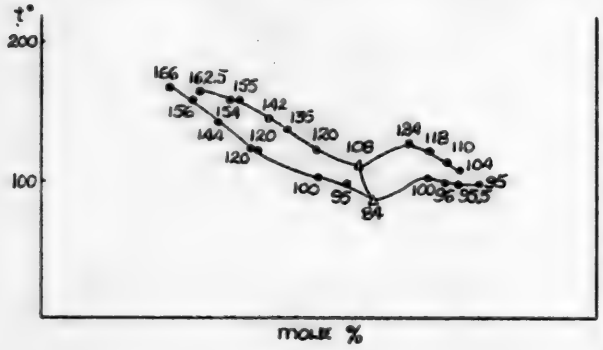

Fig. 6. Projection of the joint crystallization lines of the ternary system onto the cesium nitrate–thallium nitrate side.

This fact gives a basis for considering that the tendency of some nitrate melts toward supercooling, increase of viscosity and vitrification observed in such cases, is no other than the qualitative characteristic of the chemism appearing between the components in the melts, and the phenomena of supercooling, viscosity and vitrification are genetically connected.

It is known that for the crystallization of a substance, necessary conditions among others, is that the molecules, atoms or ions be in a definite order in the crystal lattice. The mobilities required for this were possible only under the conditions of a definite ratio between the energies of the heats of motion and the energies of the interactions of the molecules [6].

On cooling the melt, the rate of molization (a process, which is the opposite to ionization) increases, and thus the moment comes when the energy of the heat of motion becomes insufficient for the transfer of the molecules, as a result of which the viscosity of the melt increases. When the viscosity of the melt becomes so great that the motions of the atoms and atomic groups are impeded, there is orientation and coherence into crystal nuclei, and the process of crystallization sets in, slowly at first, and the melt solidifies to a vitreous mass or glass.

Fig. 7. Projection of the crystallization surface of the system on the basis of a prism.

It is necessary to assume that for the formation of the complex compounds, $Cd(NO_3)_2 \cdot 2KNO_3$, $Cd(NO_3)_2 \cdot 2RbNO_3$, $Cd(NO_3)_2 \cdot 2CsNO_3$, $Cd(NO_3)_2 \cdot 2TlNO_3$, etc., the process of crystallization of the components from the melt is considerably complicated. This also may properly explain why melts containing the nitrates of calcium and cadmium in binary or ternary combinations with the nitrates of potassium, rubidium, thallium and silver, i.e., in all cases when a chemical compound of the double salt type is formed, tend toward supercooling, have a high viscosity, and form vitreous masses only at definite concentrations of the components.

Investigating vitrification from the point of view of the concentrations of the nitrate components, we found that vitrification is affected by component concentrations which correspond to the composition of the chemical compounds formed, or correspond to the crystallization branch of these compounds on the fusibility curve, and the molecules lying adjacent to it; thus, as a rule, on the diagram of the ternary system of nitrates, the position of the area of vitrification agrees with the position of the area of crystallization of the complex compound, sometimes exceeding it only in size.

A difference was observed in the investigations of the binary systems of the nitrates of lithium, calcium and cadmium in melts. The components in the binary and ternary combinations mentioned form only eutectics. A similar phenomenon occurred in the binary and ternary systems of the nitrates of the metals of the first group of the D. I. Mendeleev periodic system, in combination with the nitrates of strontium and barium. In neither system did we observe supercooling, nor an increase of viscosity of the melt, nor vitrification. It is also interesting to observe that in such binary systems, the position of the eutectic on the fusion diagram is found to be in complete agreement with the rule that we discussed earlier [7].

Properly we turn our attention to the inadequately grounded assertion of G. Tamman [8] that the conditions promoting the transition of a substance to the vitreous state depend only on the rate of cooling, the rate of growth and the number of crystallization centers forming. In our studies it was shown that at the same rate of cooling, vitrification was not observed in all cases, but only at definite concentrations and combinations of components. In the first place, we assume that vitrification is determined by the physico-chemical nature of the components, their capacities for complex formation and association of the molecules. In connection with this, it appeared at such concentrations of the initial substances as were required for formation of complexes of the double salt type. From this point of view, vitrification is a result of complex formation of the salts in the melts and the complex particles bound to them, hamperingthe construction of the crystal lattice and the occurrence of crystallization.

SUMMARY

1. It was found that the nitrates of thallium and cesium react chemically with cadmium nitrate in melts, and form the chemical compounds: $Cd(NO_3)_2 \cdot 2TlNO_3$ having a transition point at 105°, and $Cd(NO_3)_2 \cdot 2CsNO_3$ melting at 178°.

2. It was shown that cesium nitrate gives a continuous series of solid solutions with thallium nitrate.

3. The ternary system of the nitrates of cesium, thallium and cadmium was investigated, and it was found that there are two invariant composition points: a) at 31% thallium nitrate, 17.2% cesium nitrate, 51.8% cadmium nitrate, and a m.p. of 108°; and b) at 35.5% thallium nitrate, 16.1% cesium nitrate, 48.4% of cadmium nitrate, and a m.p. of 84°.

In the system there were four areas of crystallization: cadmium nitrate, the area of crystallization of which was 22.32% of the total area of the triangle; an isomorphic mixture of the nitrates of cesium and thallium – 68.68%; the chemical compound $Cd(NO_3)_2 \cdot 2CsNO_3$ – 7.35% and the chemical compound $Cd(NO_3)_2 \cdot 2TlNO_3$ – 1.65%.

4. It was shown that in all the binary and ternary systems, containing the nitrates of the metals of the first and second groups of the D. I. Mendeleev periodic system, which enter into chemical reaction – the phenomena of supercooling, increase of viscosity and vitrification are genetically connected and appear to be qualitative manifestations of the chemism in the melts during formation of complex compounds of the double salt type.

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* See Consultants Bureau Translation, page 1421.

** See Consultants Bureau Translation, page 1357.

*** See Consultants Bureau Translation, page 1313.

REACTIONS IN MELTS OF THE NITRATES AND NITRITES OF THE METALS IN THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM

XVII. INVESTIGATION OF THE TERNARY SYSTEM OF THE NITRATES OF RUBIDIUM, CESIUM AND CALCIUM

P. I. Protsenko and Z. I. Belova

In this work, judging ffom the literature sources known to us, we have demonstrated for the first time the behavior of the nitrates of rubidium, cesium and calcium, present simultaneously in fusions. In the combination indicated, the nitrates of the metal ions are characterized by common structures, i.e., they have electron shells of the inert gas type, and therefore, they also possess an isotropism of ionic field forces.

The ions of rubidium and cesium, as univalent ions with large radii equal to 1.49 and 1.67, respectively, and characterized by substantial coefficients of polarizability – 1.49 and 2.57, generate extremely small ionic field strengths – 0.5 and 0.4 and are easily deformed in general, all the more so under such a polarizing force as is created by calcium ions.

In contrast to rubidium and cesium ions, calcium ions, as a result of their large double nuclear charge and their comparatively small ionic radius, equal to 1.06 A, form a substantial ionic field strength of 1.8 [1].

A. F. Kapustinsky and K. B. Yatsimirsky [2] showed that the thermochemical radii of the NO_3^- ions making up the anionic atmosphere remain almost unaltered, and equal approximately 1.89 A, in the different nitrates, and that because of this, the ionic field which they create is little changed; in such a case, an investigation of the interactions among the nitrates in melts may be reduced to a consideration of the interactions among the field forces of the cations.

EXPERIMENTAL

Binary systems. The binary systems $RbNO_3|CsNO_3$, $Ca(NO_3)_2|RbNO_3$ and $Ca(NO_3)_2|CsNO_3$, constituting the sides of the concentration triangle, were investigated for the first time by us.

In the binary system rubidium nitrate–cesium nitrate, the components give a continuous series of solid solutions. In the binary systems calcium nitrate–rubidium nitrate and calcium nitrate–cesium nitrate, formation of the chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ occurs.

The ternary system. In accordance with the principle following from the theory of ternary systems [3, 4], and also proceeding from the type of melting point diagrams of the binary systems, constructed on the basis of a triangle, it was possible beforehand to represent the form of the liquidus area of the ternary system for which, in the simplest case, one should expect the appearance of an area of isomorphic mixtures of rubidium and cesium nitrates, two areas of chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$, and an area of the pure component, $Ca(NO_3)_2$; moreover, this does not exclude the possibility of complications of the liquidus area, which may be expressed by the decomposition of the solid solutions, the appearance of polymorphic modifications of the pure components and the formation of new phases, particularly triple compounds, within the system.

In order to investigate the liquidus area of this system, 12 sections were studied. The first 10 sections were arranged in directions from the calcium nitrate–cesium nitrate side of the triangle to the rubidium nitrate apex; section XI was situated in a direction from the rubidium nitrate–calcium nitrate side to the cesium nitrate apex; and section XII proceeded parallel to the base of the triangle. The positions and directions of all the sections are shown in Fig. 1, and the composition transition points and the melting points corresponding to them are reported in the Table. The liquidus curves of all the sections are presented in Figs. 2, 3, 4, and 5. A projection of the liquidus area of the ternary system is shown in Fig. 6. The isotherms were carried out for every 20°. An orthogonal projection onto the rubidium nitrate–cesium nitrate side of the triangle is illustrated in Fig. 7.

From the projection of the isotherms of the liquidus areas it is evident that the system components form three crystallization areas: calcium nitrate, occupying 16.38%, the solid solutions having the chemical compositions, $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ – 20.16%, and the solid solution of rubidium nitrate and cesium nitrate – 63.46%.

TABLE

Section No.	Equimolecular per cent			M.p. of the transition points
	$RbNO_3$	$CsNO_3$	$Ca(NO_3)_2$	
I a*	37.0	3.2	59.8	212.0°
I b**	59.0	2.2	38.8	128.0
II a	35.3	6.5	58.2	112.5
II b	57.8	4.0	38.2	125.0
III a	26.3	14.9	58.8	227.0
III b	53.0	9.5	37.5	130.0
IV a	16.0	25.2	58.8	230.0
IV b	45.5	16.5	38.0	130.0
V	41.0	20.5	38.5	132.0
VI	28.0	32.5	39.5	145.0
VII	5.0	52.4	42.6	176.0
XI a	20.0	20.0	60.0	227.0
XI b	14.0	44.5	41.5	168.0

Note: Section XII was constructed from the experimental data of all the remaining sections.

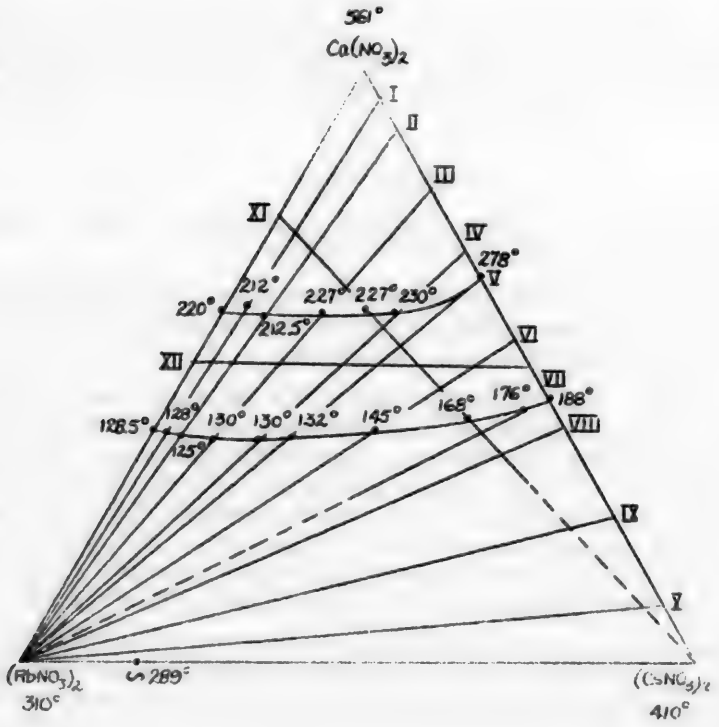

Fig. 1. Direction and position of the sections in the ternary system.

* Composition of the first transition point.

** Composition of the second transition point.

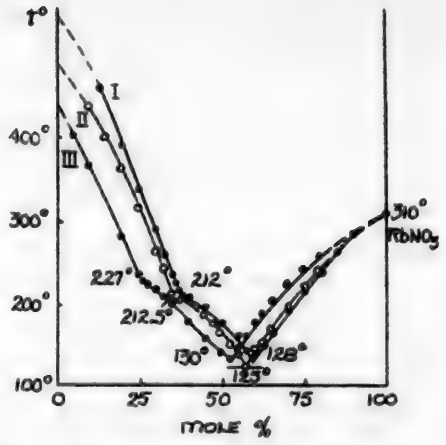

Fig. 2. Internal sections. I) 95% $Ca(NO_3)_2$ + 5% $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$; II) 90% $Ca(NO_3)_2$ + 10% $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$; III) 80% $Ca(NO_3)_2$ + 20% $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$.

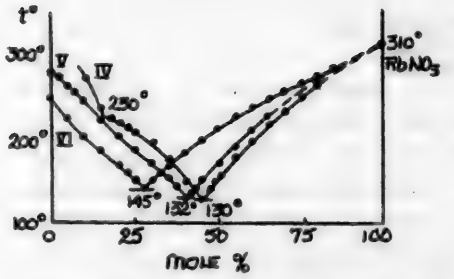

Fig. 3. Internal sections. IV) 70% $Ca(NO_3)_2$ + 30 % $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$; V) 65% $Ca(NO_3)_2$ + 35% $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$; VI) 55% $Ca(NO_3)_2$ + 45% $(CsNO_3)_2 \longrightarrow (RbNO_3)_2$.

The solid solutions formed by rubidium and cesium nitrates, appear to be extremely stable, with no indications of decomposition in the temperature interval studied.

Particular attention should be directed to the area of solid solutions having the chemical combinations $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$, which represent wide bands (zones), separating the triangle into three parts. As a result, a "zonal" type of structural diagram is obtained for the ternary system. A similar type of ternary system was described earlier by one of us, together with N. P. Popovskaya [5].

It should be noted that the indices of refraction, which generally characterize the physico-chemical and crystallo-optical nature of a substance, in the present case of the nitrates of rubidium, cesium and calcium in particular, are very close together, and equal 1.52, 1.55 and 1.49, respectively.

It would be possible, proceeding from the values of the indices of refraction, to expect to obtain solid solutions also in the rubidium nitrate–calcium nitrate and cesium nitrate–calcium nitrate systems. However, with such a combination of components, a second factor appears – the large polarizing action of the calcium ions toward rubidium and cesium ions. The latter are readily deformed, and as a result of the total action of stationary, induced and temporary dipoles, the chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ are formed. As a result of the isomorphism of rubidium and cesium nitrates, the compounds, $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ should also be isomorphic. These complexes, in turn, form a continuous series of solid solutions, the crystallization areas of which are represented in the zonal ternary system (Fig. 6).

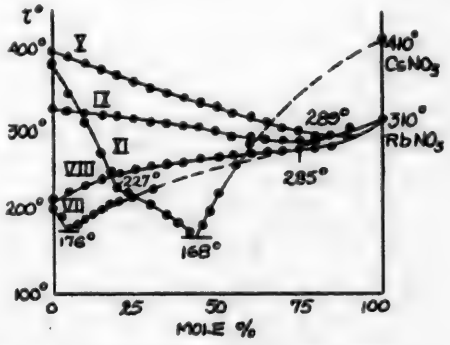

Fig. 4. Internal sections. VII) 45% $Ca(NO_3)_2$ + 55% $(CsNO_3)_2 \rightarrow (RbNO_3)_2$; VIII) 40% $Ca(NO_3)_2$ + 60% $(CsNO_3)_2 \rightarrow (RbNO_3)_2$; IX) 25% $Ca(NO_3)_2$ + 75% $(CsNO_3)_2 \rightarrow (RbNO_3)_2$; X) 10% $Ca(NO_3)_2$ + 90% $(CsNO_3)_2 \rightarrow (RbNO_3)_2$; XI) 75% $Ca(NO_3)_2$ + 25% $(RbNO_3)_2 \rightarrow (CsNO_3)_2$.

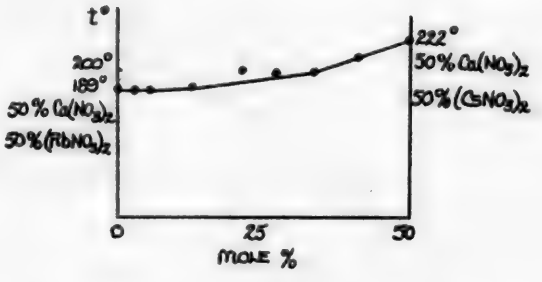

Fig. 5. Internal section XII. 50% $Ca(NO_3)_2$ + 50% $(RbNO_3)_2$ – 50% $Ca(NO_3)_2$ + 50% $(CsNO_3)_2$.

The facts stated permit one to express the following assumption in general form: if the two isomorphic substances A and B enter separately into chemical reaction with component C, and form the compounds AC and BC, then the latter also will be isomorphic. This rule is confirmed by the appearance in the liquidus areas, of solid solution areas corresponding to them. On the other hand, obtaining for the liquidus area of the ternary system a single solid solution area, the formation of a double chemical compound, would result in their isomorphism.

If the behavior of calcium nitrate in aqueous solutions and in melts is compared, then in those cases as in others, the calcium ions appear to have a distinct tendency toward complex formation. However, in polar solvents like water, and at low reaction temperatures (having in mind ordinary temperature) more favorable conditions are created for complex formation. In particular, under such conditions, the crystalline tetra-hydrate of calcium nitrate forms.

In melts, in ionic liquid environments, and at high reaction temperatures, there is a considerable increase of the kinetic energies of the ions, conditions for coordination become less favorable, and therefore, fewer characteristic complexes are produced.

Another distinguishing characteristic of the ternary system Rb, Cs, Ca $\|NO_3$ is vitrification, observed during its investigation. Both in the binary systems $Ca(NO_3)_2 | RbNO_3$ and $Ca(NO_3)_2 | CsNO_3$ along the crystallization branches of the chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ and in the ternary system Ca, Rb, Cs $\| NO_3$ in the regions adjacent to these compounds, even with energetic stirring of the melt, with seeding, and with slow cooling, an increase of viscosity, supercooling and vitrification took place. It is characteristic both here and in many systems described earlier, that vitrification is observed only when, other conditions remaining equal, the components react chemically. Vitrification in the nitrate systems, in the first place, depended on the physicochemical nature of the components. One should consider it as a qualitative manifestation of chemical interaction among them. The increase of viscosity and the occurrence of supercooling are forefunners of vitrification, are genetically connected to the latter, and in turn appear to be external manifestations of the metastable state of the system, which differs from a thermodynamically unstable system; therefore, under favorable conditions, that is: "training" • the melt, exposing it to temperatures close to the crystallization temperature, energetic agitation and rubbing the walls of the vessel with a stirring rod, by seeding, by eliminating superheating, and by slowing the rate

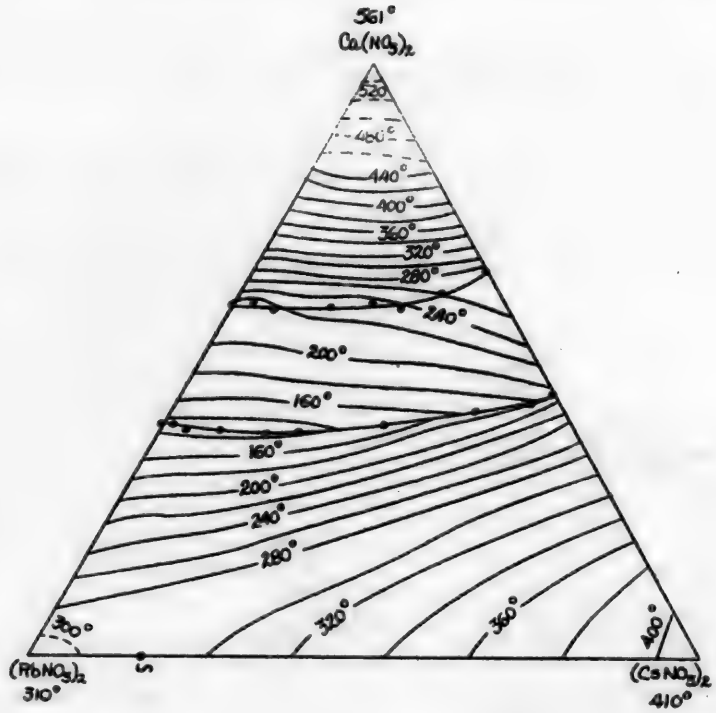

Fig. 6. Projection of the crystallization area of the system on the basis of a triangle.

• By this term is meant a repeated heating and cooling of a melt of the same composition.

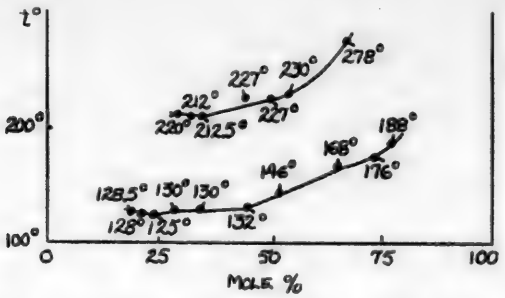

Fig. 7. Orthogonal projection of the curve of joint crystallization onto the $RbNO_3 - CsNO_3$ side.

of cooling, crystals appear, and the melt crystallizes. Under such conditions the potential energy of the molecules of the chemical compounds decreases to minimum values, and the system changes from the metastable to the stable condition. Unusual forcing [6] of the crystallization of the components produces complexities and bulkinesses in the $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$ molecules, impeding their proper arrangement in the crystal lattices in the fusion; moreover, the association of the molecules at temperatures close to the crystallization temperature, is of important significance.

SUMMARY

1. We confirmed the formation in melts of the chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$, which we established earlier.

2. We obtained a diagram for the ternary system of rubidium, cesium and calcium nitrates, characterized by the presence of zones of formation of isomorphic mixtures of the chemical compounds $Ca(NO_3)_2 \cdot RbNO_3$ and $Ca(NO_3)_2 \cdot CsNO_3$.

3. It was shown that if two isomorphic components, for example A and B enter separately into chemical reaction with component C, and form the compounds AC and BC, the latter also will be isomorphic.

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* See Consultants Bureau Translation, page a-665.

** See Consultants Bureau Translation, page 1313.

PHYSICO-CHEMICAL INVESTIGATION OF THE REACTION OF TITANIUM TETRACHLORIDE WITH THE ESTERS OF MONOBASIC ACIDS

V. REACTION OF TITANIUM TETRACHLORIDE WITH n-PROPYL ACETATE AND n-BUTYL ACETATE

O. A. Osipov, Yu. A. Lysenko and E. K. Akopov

Our previous investigations [1, 2, 3] showed that titanium tetrachloride reacts with esters of monobasic acids, with the formation in the liquid phase of compounds having the compositions $TiCl_3 \cdot E$ and $TiCl_4 \cdot 2E$ (where E is the ester molecule); the compound of the first type is more characteristic of the complexes of titanium tetrachloride with acetates, whereas tin tetrachloride reacts with the double molecule of the ester.

We attempted to account for this fact by the differences in the values of the tetrahedral covalent radii of titanium and tin, and also indicated a possible steric hindrance, apparently arising in the case of the bulky alcohol radicals. In order to elucidate the nature of the effect of the alcohol radical in the acetate molecule on its reaction with titanium tetrachloride, we studied the systems titanium tetrachloride–n-propyl acetate and titanium tetrachloride–n-butyl acetate, with respect to viscosity, density and electrical conductivity.

In order to obtain more conclusive data on the chemism between the components studied, we also determined the heat of mixing for the system titanium tetrachloride–n-propyl acetate. The results of the determination of the heat of mixing for the system titanium tetrachloride–n-butyl acetate were published earlier [4]. The methods of measuring the specified properties were described in previous reports [1, 4].

EXPERIMENTAL

System titanium tetrachloride–n-propyl acetate. For the investigation, c.p. titanium tetrachloride and n-propyl acetate were used. The normal propyl acetate, after prolonged drying over calcium chloride, was distilled twice. The fraction having a b.p. of 101.3-102°, d_4^{20} 0.8859, n_D^{20} 1.3842 was used for the work.

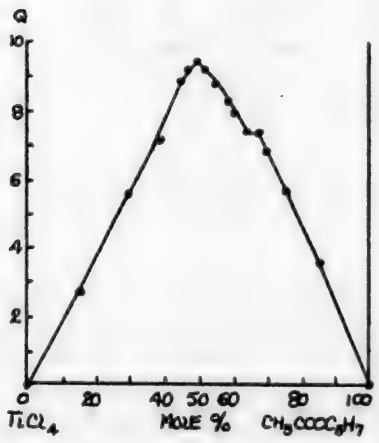

Fig. 1. Heats of mixing of the system $TiCl_4$–$CH_3COOC_3H_7$.

In Fig. 1 are the results of the measurement of the heats of mixing at 23°, expressed in kcal per mole of mixture. The determination of the heat of mixing for the present system at 23° by the method used [4] was possible because of the strong supercooling of the mixture during its formation. On the heat of mixing curve there is a sharply expressed maximum corresponding to an equimolecular ratio of the components. Moreover, there is a break on the curve corresponding to 64 mole % of n-propyl acetate, for which the reproducibility in this region decreases somewhat. The viscosity, density and electrical conductivity were measured at 70 and 80°. Selection of the temperatures specified was determined by the appearance of crystals at temperatures below 70°, and by partial resinification of the fusions at 80-90°. In Fig. 2 (I and II) are the results of the viscosity measurements, expressed in centipoises. On the viscosity isotherms there are sharply expressed maxima, at 52 mole % of n-propyl acetate at 70° and at 54 mole % at 80°. The observed maxima on the viscosity isotherms, displaced along the composition axis by a rise in temperature, indicate the formation in the system of the compound $TiCl_4 \cdot CH_3COOC_3H_7$, dissociated in the liquid phase. The results of the calculation of the relative and absolute temperature coefficients of the viscosity, presented in Fig. 2 (III and IV), confirm the formation of the compound $TiCl_4 \cdot CH_3COOC_3H_7$ in the system. Besides the maxima on the curves of the absolute and relative temperature coefficients of viscosity, corresponding almost to the composition of the 1:1 compound, on the branch of the curve adjacent to the ester, there is a break corresponding to 66 mole % of n-propyl acetate. The latter break is especially outstanding on the curve of the relative temperature coefficient of the viscosity (Fig. 2, III).

In Fig. 3 are the results of the density measurements at 70 and 80° (I and II). A considerable reduction, occurring at 40-50 mole % of n-propyl acetate, sharply indicates the expressed chemism between the components; however, on the density curves, both points indicating the formation of compounds are absent, which might have explained the low sensitivity of the density as a property.

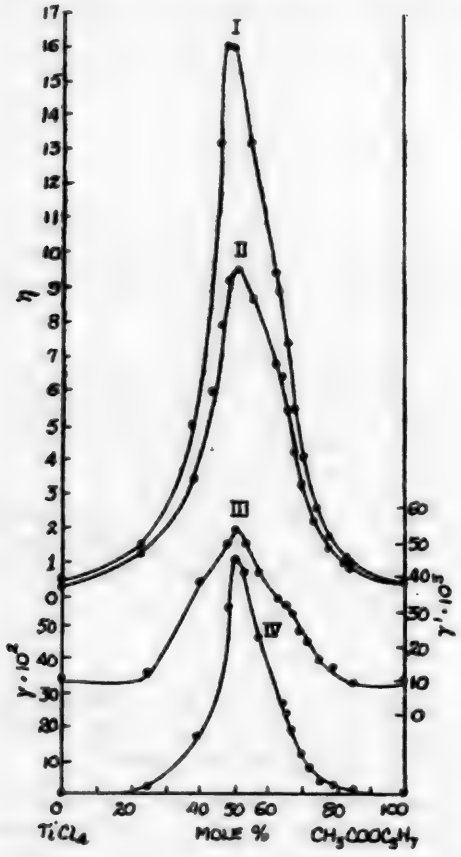

Fig. 2. Viscosity isotherms of the system $TiCl_4-CH_3COOC_3H_7$. I) 70°; II) 80°; III) relative temperature coefficient of viscosity; IV) absolute temperature coefficient of viscosity.

The results of the electrical conducitivity measurements presented in Fig. 4 confirmed the results of the preceding determinations. The electrical conductivity isotherms have 3 maxima and 2 minima, corresponding to 52-mole % n-propyl acetate and 68 mole % n-propyl acetate, which confirms the formation in the system of the compounds: $TiCl_4 \cdot CH_3COOC_3H_7$ and $TiCl_4 \cdot 2CH_3COOC_3H_7$ (Fig. 4, II and III), which were dissociated in the liquid phase. Apparently, the considerable decrease of the viscosity with an increase of the temperature causes the smoothing out of the minima observed on the electrical conductivity isotherms at 80°. In Fig. 4 (V and IV) are presented the curves of the absolute and relative temperature coefficients of the electrical conductivity, the form of which confirms the formation in the system of the two compounds indicated above.

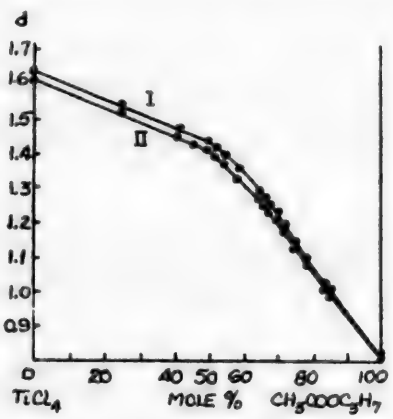

Fig. 3. Density isotherms of the system $TiCl_4-CH_3COOC_3H_7$. I) 70°; II) 80°.

The electrical conductivity curve depicted in Fig. 4 (I), calculated by us for 70°, proceeds through a sharp maximum, corresponding almost to an equimolecular proportion of the components, and confirming once again the formation of the compound $TiCl_4 \cdot CH_3COOC_3H_7$.

Thus, comparison of the results of the study of all the properties considered above proves that in the system titanium tetrachloride–n-propyl acetate, together with the compound $TiCl_4 \cdot CH_3COOC_3H_7$, there occurs the formation of the compound of the composition $TiCl_4 \cdot 2CH_3COOC_3H_7$, which is dissociated in the liquid phase.

System titanium tetrachloride–n-butyl acetate. For the investigation, we used c.p. n-butyl acetate, dried for a long time over calcium chloride, after which it was distilled twice, and for the work the fraction boiling within the range 124.8-125.1°, d_4^{20} 0.8818, n_D^{20} 1.3950, was taken.

The viscosity, density and electrical conductivity were measured at 70, 80, 85 and 90°. These temperatures were chosen on the same basis as those for the preceding systems. The results of the viscosity measurements are presented in Fig. 5 (I, II, III, IV). The viscosity isotherms proceed through maxima, corresponding to 55 mole % of n-butyl acetate, which indicates the formation of a compound having the composition $TiCl_4 \cdot CH_3COOC_4H_9$, which is dissociated in the liquid phase. An increase of the temperature leads to considerable dissociation of the compound formed, which is indicated by a smoothing out of the maxima observed on the viscosity isotherms with a rise in temperature. The results of the calculations of the absolute and relative temperature coefficients of the

viscosity, given in Fig. 5 (VI and V), confirm the formation of the indicated compound in the system. The curve of the absolute temperature coefficient has a maximum corresponding to 52 mole % of n-butyl acetate. At 60 mole % of n-butyl acetate, a sharp break is observed on the curve. On the curve of the relative temperature coefficient of viscosity there was a similar break, which indicated the formation in the system of a second com-

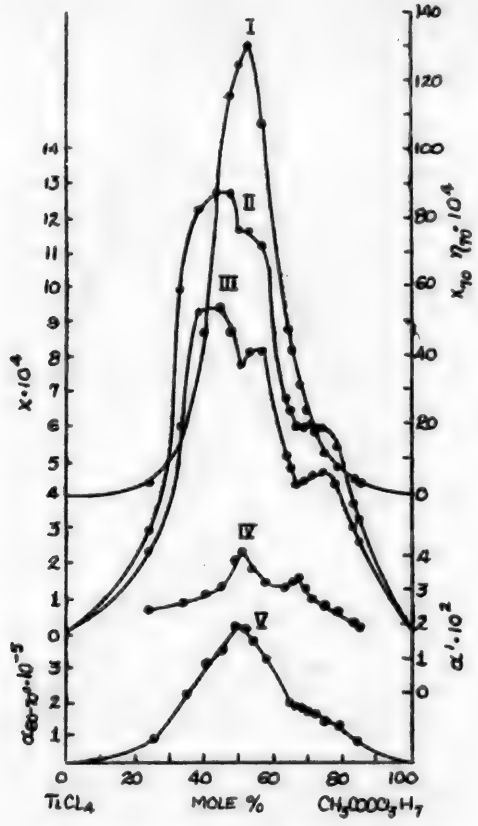

Fig. 4. Electrical conductivity isotherms of the system $TiCl_4-CH_3COOC_3H_7$. I) Calculated electrical conductivity; II) 80°; III) 70°; IV) relative temperature coefficient of electrical conductivity; V) absolute temperature coefficient of electrical conductivity.

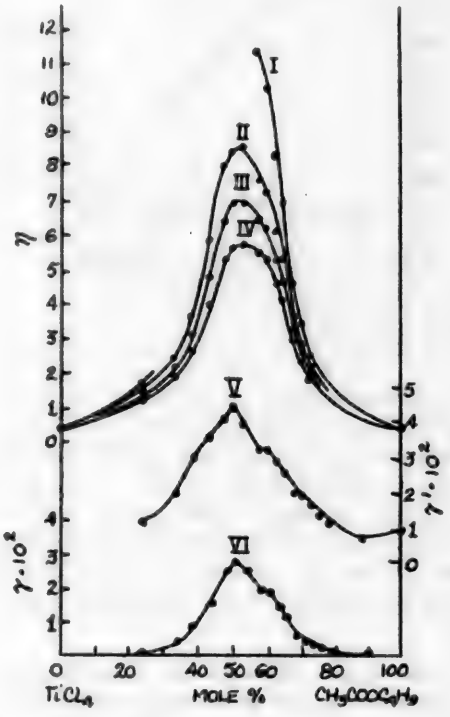

Fig. 5. Viscosity isotherms of the system $TiCl_4-CH_3COOC_4H_9$. I) 70°; II) 80°; III) 85°; IV) 90°; V) relative temperature coefficient of viscosity ($\gamma'_{90-85°}$); VI) absolute temperature coefficient of viscosity ($\gamma_{90-85°}$).

pound of composition $TiCl_4 \cdot 2CH_3COOC_4H_9$, which was highly dissociated in the liquid phase.

The results of the determination of the density at 80° are presented in Fig. 6. Because of the negligible temperature coefficient of the density, we did not carry out isotherms at 70, 85 and 90°, since they almost coincide with each other. It follows from Fig. 6 that in the given system a rather appreciable decrease in density occurs in the region of 45-60 mole % n-butyl acetate, which confirms the significant chemism between the components.

The results obtained from the measurements of the specific electrical conductivity are shown in Fig. 7. The electrical conductivity isotherms at 80, 85 and 90° (Fig. 7, III, II, I) represent curves having two maxima at 45 and 52 mole % n-butyl acetate, and a minimum corresponding to 50 mole % n-butyl acetate. On the specific conductivity isotherm at 80° there is a break corresponding to 67 mole % n-butyl acetate. Such a break is especially noticeable on the completed part of the 70° isotherm (Fig. 7, IV). On the specific electrical conductivity isotherm at 85° in the region corresponding to the composition of the compound $TiCl_4 \cdot 2CH_3COOC_4H_9$, there is only a discontinuity, which indicates the dissociation of this compound at 85°. The effect of the temperature on the dissociation of the compound $TiCl_4 \cdot 2CH_3COOC_4H_9$ is especially indicated by the character of the isotherm at 90°, a considerable smoothing out of the discontinuity being observed, at 67 mole % of n-butyl acetate. The results of the calculation of the absolute and relative temperature coefficients are given in Fig. 7 (VII and VI). Here also are given the electrical conductivity results. The curves of the absolute and relative temperature coefficients of the specific electrical conductivity have two sharply expressed maxima, corresponding to 50 mole %

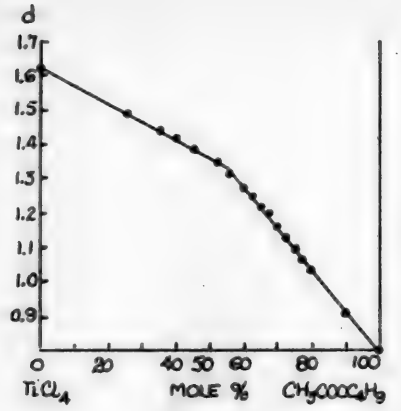

Fig. 6. Density isotherm of the system $TiCl_4 - CH_3COOC_4H_9$.

n-butyl acetate, and 67 mole % n-butyl acetate, which confirms the formation in the system of the two compounds of the compositions: $TiCl_4 \cdot CH_3COOC_4H_9$ and $TiCl_4 \cdot 2CH_3COOC_4H_9$. The electrical conductivity curve, calculated for 85°, passes through a maximum corresponding to 52 mole-% n-butyl acetate, which also indicates the formation in the system of a compound of 1:1 composition (Fig. 7, V).

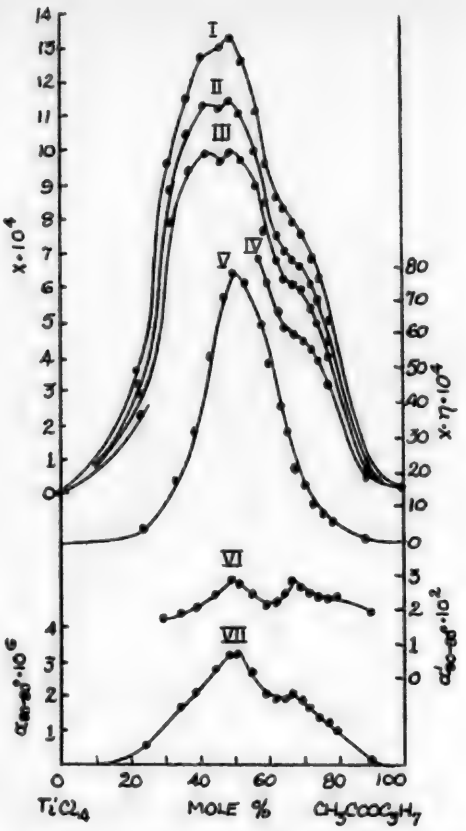

Fig. 7. Electrical conductivity isotherms of the system $TiCl_4 - CH_3COOC_4H_9$. I) 90°; II) 85°; III) 80°; IV) 70°; V) calculated electrical conductivity for 85°; VI) relative temperature coefficient of electrical conductivity ($\alpha'_{90-80°}$); VII) absolute temperature coefficient of electrical conductivity ($\alpha_{90-80°}$).

The results obtained in the investigation of the viscosity, density and electrical conductivity of the system titanium tetrachloride–n-butyl acetate, enable us to conclude that in the system the two compounds, $TiCl_4 \cdot CH_3COOC_4H_9$ and $TiCl_4 \cdot 2CH_3COOC_4H_9$, which dissociate in the liquid phase, are formed and the latter compound $TiCl_4 \cdot 2CH_3COOC_4H_9$ displays a comparatively lower thermal stability. This conclusion is found to be in complete agreement with the results of the determination of the heat of mixing for the present system, which we carried out somewhat earlier [4].

As our experimental data show, titanium tetrachloride reacts with n-butyl acetate and n-propyl acetate with the formation of compounds of the type: $TiCl_4 \cdot E$ and $TiCl_4 \cdot 2E$; moreover, the thermal stability of the compound of the second type is shown to be somewhat less than that of the compound $TiCl_4 \cdot E$ and decreases according to the degree of complexity of the alcohol radical in the ester molecule. We assume that the considerable decrease of the thermal stability, on transition to the C_5H_{11} radical leads to a more complete dissociation at 60-70° of the compound $TiCl_4 \cdot 2CH_3COOC_5H_{11}$, than could be accounted for by the formation in the liquid phase of only the compound $TiCl_4 \cdot CH_3COOC_5H_{11}$, in the case of the reaction of titanium tetrachloride with isoamyl acetate [1]. Such a dissociation, apparently, occurs at 97-102° for the reaction of titanium tetrachloride with ethyl acetate [3].

Thus, the results of our investigation confirm the hypothesis that we advanced earlier.

SUMMARY

1. The viscosity, density and electrical conductivity for the system titanium tetrachloride–n-propyl acetate were measured at 70 and 80°, and for the system titanium tetrachloride–n-butyl acetate, at 70, 80, 85 and 90°.

2. The heat of mixing for the system titanium tetrachloride–n-propyl acetate was determined.

3. It was found that titanium tetrachloride forms compounds of the composition $TiCl_4 \cdot CH_3COOC_3H_7$ and $TiCl_4 \cdot CH_3COOC_4H_9$ with n-propyl acetate and n-butyl acetate.

4. It was shown that titanium tetrachloride yields, with n-propyl acetate and n-butyl acetate, together with compounds of the $TiCl_4 \cdot E$ type, also compounds of the $TiCl_4 \cdot 2E$ type, the stability of which decrease with the complexity of the alcohol radical in the ester molecule.

5. A new confirmation was obtained for the hypothesis that we advanced earlier with respect to the effect of the alcohol radical, in the ester molecule, on the composition of the compounds obtained.

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ELECTRICAL CONDUCTIVITY OF THE SYSTEMS ALUMINUM CHLORIDE–ACETAMIDE–NITROBENZENE AND ALUMINUM CHLORIDE–UREA–NITROBENZENE

B. Ya. Rabinovich and A. G. Ponomarenko

Investigation of nitrobenzene solutions of aluminum chloride with acetamide and urea, by the method of measuring the specific gravities and viscosities [1], and also by cryoscopic measurements of the system aluminum chloride–acetamide–nitrobenzene [2], showed that aluminum chloride in nitrobenzene solution with acid amides forms complex compounds of the compositions $AlCl_3 \cdot CH_3CONH_2$ and $AlCl_3 \cdot CO(NH_2)_2$.

Nitrobenzene solutions of aluminum chloride conduct the electric current. The electrical conductivities of these solutions, within a concentration range of 0-25% by weight of aluminum chloride, were measured at 18° by V. A. Plotnikov and I. M. Podorvan [3], and at 25° by V. A. Plotnikov and R. G. Vaisberg [4]. The specific electrical conductivity isotherm develops a maximum at a concentration of approximately 14% aluminum chloride. The specific electrical conductivity, corresponding to the maximum, was equal to $1.5 \cdot 10^{-3}\ \Omega^{-1} \cdot cm^{-1}$. The molecular electrical conductivity increases with dilution of the solution, approaching the limiting value of $4.5\Omega^{-1} \cdot cm^2$. .

The electrical conductivity of the system aluminum chloride–nitrobenzene depended on the formation of an ionized nitrobenzene complex of aluminum chloride. According to data from thermal analysis, cited by B. N. Menshutkin [5], aluminum chloride forms two compounds, $AlCl_3 \cdot 2C_6H_5NO_2$ having a m.p. of 25.5° and $AlCl_3 \cdot C_6H_5NO_2$, having a m.p. of 90°, with nitrobenzene.

Thus, complex formation in the nitrobenzene solution is probably connected with the decomposition of the nitrobenzene complex and replacement of nitrobenzene in the internal coordination sphere, or with the formation of a triple complex compound.

From this point of view, it is of interest to investigate the changes of the electrochemical properties of nitrobenzene solutions on addition of a third component, which enters into complex formation with aluminum chloride.

Such investigations were carried out by V. A. Plotnikov and I. M. Podorvan [3] for the system aluminum chloride–potassium chloride–nitrobenzene, by A. M. Ruban [6] for the system aluminum chloride–sodium chloride–nitrobenzene, and by Van Dyke and Crawford for the system containing methyl ether, methyl alcohol or acetone [7], and also pyridine or ammonia [8].

Addition of potassium or sodium chloride to the nitrobenzene solution of aluminum chloride produces approximately a 2-10 fold increase of the specific electrical conductivity, depending on the concentration of the alkali metal halide.

As to the system studied by Van Dyke and Crawford [7, 8], the addition of ether, alcohol or acetone produced a decrease of the electrical conductivity of the solution up to a molar ratio of organic addend to $AlCl_3$ equal approximately to unity. On addition of pyridine or ammonia, the specific electrical conductivity increased slightly at first, but on reaching a molar ratio equal approximately to unity, a sharp increase of the electrical conductivity occurred; in the system with pyridine, the electrical conductivity isotherm developed a maximum at a molar ratio of $C_5H_5N:AlCl_3 = 2$. The system with ammonia was studied up to a molar ratio of $NH_3:AlCl_3 = 1.3$, since a further increase of the ammonia concentration causes precipitation of the complex.

We studied the effect of acetamide and urea on the electrical conductivities of nitrobenzene solutions of aluminum chloride.

EXPERIMENTAL

The starting materials were: aluminum chloride, acetamide, urea and nitrobenzene, purified in the same way as described earlier [1].

TABLE 1

System Aluminum Chloride–Acetamide–Nitrobenzene
(Concentration of aluminum chloride 2.6%)

No.	CH_3CONH_2 / $AlCl_3$ (moles)	Specific electrical conductivity $\kappa \cdot 10^4\ \Omega^{-1} \cdot cm^{-1}$		Temperature coefficient of electrical conductivity $\alpha \cdot 10^3$
		25°	35°	
1	–	5.0	4.8	−4.0
2	0.206	6.2	6.3	1.6
3	0.401	6.6	6.8	3.0
4	0.506	7.1	7.4	4.2
5	0.611	7.4	7.9	6.8
6	0.803	8.3	9.0	8.4
7	0.909	11.4	12.5	9.6
8	1.002	12.3	13.4	8.9
9	1.107	16.6	18.0	8.4
10	1.230	19.5	21.2	8.7

The electrical conductivity was determined in a vessel having a ground-glass stopper and platinized platinum electrodes. The measurements were carried out by the usual method, using a tube generator with an optical indicator. The solutions were prepared by the method of addition. To nitrobenzene solutions of aluminum chloride of constant concentrations, different weighed portions of acetamide or urea were added. Because of the sensitivity of this system to moisture, for each determination amide was added to a new portion of solution.

Acetamide and urea were difficultly soluble in nitrobenzene, but in solutions of aluminum chloride their solubilities increased in proportion to the aluminum chloride content. In our experiments we added amide up to a molar ratio of RNH_2*:$AlCl_3$ = 1.2. The electrical conductivity of the system aluminum chloride–acetamide–nitrobenzene was determined for two concentrations of aluminum chloride: 2.6% by weight at 25 and 35°, and 11.0% by weight at 18, 25 and 35°.

The results of the measurements are presented in Tables 1 and 2, and graphically in Fig. 1.

TABLE 2

System Alumimum Chloride–Acetamide–Nitrobenzene (Concentration of aluminum chloride 11.0%)

No.	CH_3CONH_2 / $AlCl_3$ (moles)	Specific electrical conductivity $\kappa \cdot 10^4\ \Omega^{-1} \cdot cm^{-1}$			Temperature coefficient of electrical conductivity at 35-18° $\alpha \cdot 10^3$	Specific electrical conductivity at 18°, corrected for viscosity $\kappa' \cdot 10^4\ \Omega^{-1} \cdot cm^{-1}$
		18°	25°	35°		
1	–	13.9	13.9	13.6	− 1.3	13.9
2	0.201	14.4	14.8	14.9	2.0	14.2
3	0.403	14.9	15.7	16.5	6.3	14.0
4	0.500	15.1	16.0	17.2	8.2	13.1
5	0.602	15.5	16.6	18.4	11.0	13.1
6	0.805	16.8	18.7	21.5	16.5	13.8
7	0.901	17.7	20.0	23.6	19.6	14.2
8	1.000	21.2	24.0	28.0	18.9	17.9
9	1.120	28.0	31.9	37.0	18.9	24.9
10	1.201	33.0	37.2	43.5	18.7	30.4

We determined the electrical conductivity of the system aluminum chloride–urea–nitrobenzene at one concentration of aluminum chloride, equal to 7% by weight at both 18 and 30°. The results of the measurements are presented in Table 3 and in Fig. 2.

We calculated the temperature coefficient of the electrical conductivity by the formula $\alpha = \frac{\kappa_{t_2} - \kappa_{t_1}}{\kappa_{t_1}(t_2 - t_1)}$, where κ_{t_2} and κ_{t_1} are the electrical conductivites at temperatures t_2 and t_1 for $t_2 > t_1$.

In the tables are also given values of the specific electrical conductivities at 18°, corrected for viscosity, calculated from the formula $\kappa' = \kappa \cdot \frac{\eta_1}{\eta_0}$, where κ' and κ are the conductivity, corrected for viscosity, and the measured conductivity, respectively, η_0 is the viscosity of the nitrobenzene solution of aluminum chloride, and η_1 is the viscosity of the same solution after addition of amide. The viscosity data for this system were presented earlier [1].

* RNH_2 = acetamide or urea.

TABLE 3

System Aluminum Chloride–Urea–Nitrobenzene (Concentration of aluminum chloride 7%)

No.	$CO(NO_2)_2$ / $AlCl_3$ (moles)	Specific electrical conductivity $\kappa \cdot 10^4\ \Omega^{-1} \cdot cm^{-1}$		Temperature coefficient of electrical conductivity $\alpha \cdot 10^3$	Specific electrical conductivity at 18°, corrected for viscosity $\kappa' \cdot 10^4$
		18°	30°		
1	–	11.4	10.8	– 4.4	11.4
2	0.200	11.8	11.7	– 0.7	11.9
3	0.400	12.1	12.7	4.1	12.0
4	0.502	12.2	13.3	7.5	12.0
5	0.600	12.2	13.7	10.3	11.7
6	0.801	13.2	15.4	13.9	12.6
7	0.907	14.1	17.0	17.1	13.7
8	1.000	18.2	21.9	16.9	17.9
9	1.103	24.0	28.9	17.0	25.2

DISCUSSION OF RESULTS

As is evident from the data given in Fig. 1 and 2, the nature of the isotherms in both systems is identical. On addition of the amide, the specific electrical conductivity at first increased very slowly, and only at an amide concentration of 0.9–1.0 mole per 1 mole of $AlCl_3$ did a sharp increase of the electrical conductivity occur.

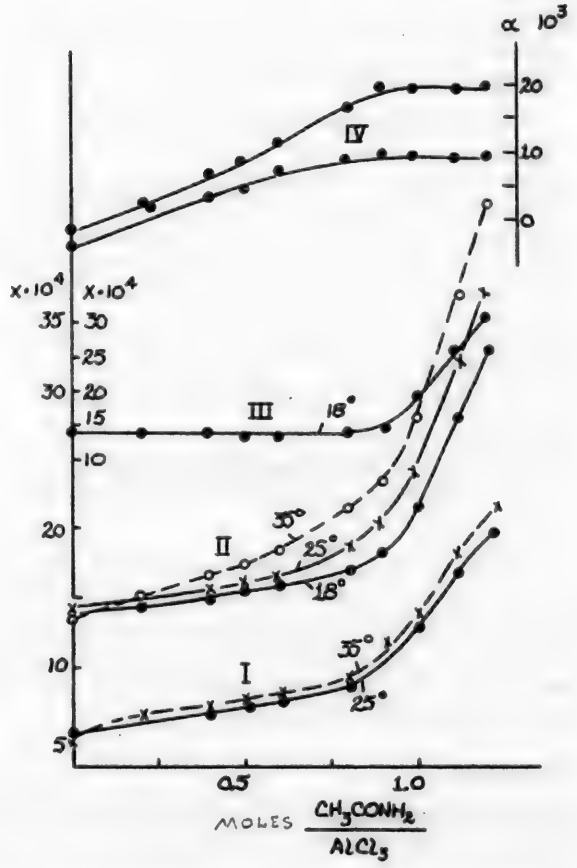

Fig. 1. Specific electrical conductivity of the system $AlCl_3$–CH_3CONH_2–$C_6H_5NO_2$. I) 2.6% $AlCl_3$; II) 11.0% $AlCl_3$; III) specific electrical conductivity; IV) temperature coefficient of electrical conductivity.

The initial insignificant increase of the electrical conductivity depended on a decrease of the viscosity of the system. After correction of the specific electrical conductivity for viscosity, the isotherms acquired a linear character, and only at a molar ratio of the components equal to approximately 1:1, did a sharp increase of the electrical conductivity and viscosity of the system occur.

On addition of amide, the temperature coefficient of the electrical conductivity increased, reaching a maximum at a molar ratio of amide : $AlCl_3 \approx 0.9$–1.0, after which it remained practically constant.

The character of the electrical conductivity isotherms confirmed the conclusion which we advanced on the basis of a study of these systems by other physico-chemical methods of analysis [1, 2], concerning the formation in the system of compounds having the compositions $AlCl_3 \cdot CH_3CONH_2$ and $AlCl_3 \cdot CO(NH_2)_2$.

The complex compounds of aluminum chloride with acetamide and urea were more stable than the nitrobenzene complexes. While the temperature coefficient of the nitrobenzene solution of aluminum chloride was negative, the formation of the amide complex was accompanied by a change of sign of the temperature coefficient.

The decrease of the electrical conductivity of the solution of aluminum chloride with an increase of temperature was connected with the decomposition of the nitrobenzene complex. In the presence of acetamide or urea, the replacement of nitrobenzene in the internal coordination sphere, in connection with the formation of a more stable

complex, occurred. Apparently, this should account for the decrease of the viscosity of the nitrobenzene solutions of aluminum chloride after addition of acetamide or urea to them.

The factors determining the viscosity seemed to be the size and mass of the molecule. The simple addition of amide molecules to nitrobenzene compounds of aluminum chloride would have led to a considerable increase of the sizes of the molecules, and consequently, also to an increase of the viscosity of the system. The replacement of the nitrobenzene molecule (M 113) by the almost half-as-heavy molecules of acetamide or urea (M ~ 60) probably also causes a change in the viscosity of the system

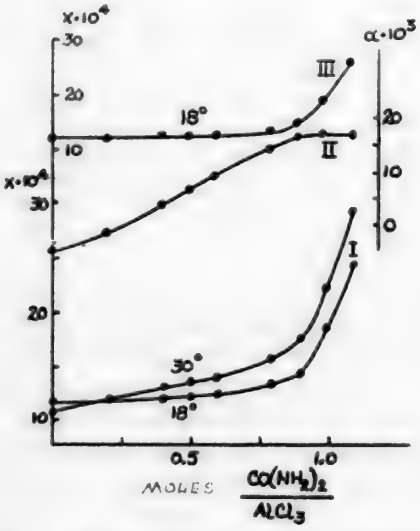

Fig. 2. The system $AlCl_3-CO(NH_2)_2-C_6H_5NO_2$. I) Specific electrical conductivity; II) temperature coefficient of the electrical conductivity; III) specific electrical conductivity, corrected for viscosity.

This, naturally, did not exclude solvation of the evolved more stable amide complexes by the polar nitrobenzene molecule.

The electrochemical investigations of nitrobenzene solutions of aluminum chloride, carried out by Van Dyke and Crawford [8, 7], showed that not only pyridine and ammonia, but also such addends as methyl ether, methyl alcohol and acetone, form more stable compounds with aluminum chloride, than does nitrobenzene.

Apparently, a complete analogy exists between the stabilities of complex compounds of the aluminum halides and of magnesium halides, which were investigated at length by B. N. Menshutkin. The identical electronic structures of the magnesium and aluminum ions and the closeness of their chemical properties, in accordance with their positions in the periodic system, lay down the conditions also for the similarity of the properties of their molecular compounds.

According to B. N. Menshutkin [9], the stability of the magnesium halide compounds decreases in the series: urea > > water > aniline, acetamide > methyl alcohol > ethyl alcohol > acetone > ethyl ether. There is approximately the same order of stabilities of the complex compounds of the aluminum halides. Urea complexes of aluminum salts were obtained by crystallization from aqueous solutions [10].

B. N. Menshutkin [9] accounted for the stability of the molecular compounds with acetamide and urea by the presence of the amide group NH_2, and the bonding of the complex-former with the addend through nitrogen. Werner [11] assumed that in the amide complexes, bonding was accomplished through the carbonyl oxygen.

Comparing the electrochemical properties of nitrobenzene solutions of aluminum chloride with different nitrogen- and oxygen-containing addends, we found that systems containing acetamide or urea are similar in their properties to solutions containing ammonia or pyridine, but are different from systems with alcohol, ether and acetone.

The specific electrical conductivity isotherms of solutions of aluminum chloride in nitrobenzene, containing alcohol, ether or acetone, pass through a minimum, while the electrical conductivity isotherms of solutions containing acetamide and urea do not develop minima, but, like systems with ammonia and pyridine, increase sharply at a molar ratio of the addend to $AlCl_3$ equal approximately to unity. To a certain extent, this similarity in electrochemical properties seems to confirm the point of view of B. N. Menshutkin concerning the bonding of the complex-former to the addend in the amide complex through the nitrogen of the amide group.

SUMMARY

1. The specific electrical conductivity of the system aluminum chloride–acetamide–nitrobenzene was determined at 18, 25 and 35°; the specific electrical conductivity of the system aluminum chloride–urea–nitrobenzene was determined at 18 and 30°.

2. The specific electrical conductivity at first increased insignificantly in proportion to the amount of acetamide or urea added, but at a concentration of 0.9-1.0 mole of amide per 1 mole of $AlCl_3$, the electrical conductivity increases sharply.

3. The temperature coefficient of the electrical conductivity developed a maximum at a molar ratio of $AlCl_3$: amide = 1, and remained practically constant on further increase of the concentration of the amide.

4. It was shown that in nitrobenzene solutions, acetamide and urea formed complex compounds of 1:1 composition with aluminum chloride, which are more stable than the nitrobenzene complexes of aluminum chloride.

5. We drew an analogy between the stability of the complex compounds of magnesium halides and those of aluminum halides. The problem of the nature of the bonding of the acid amide to the complex-former was discussed.

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REDUCTION OF m-NITROBENZENESULFONIC ACID AT THE DROPPING MERCURY CATHODE

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At the dropping mercury cathode, reduction of a series of organic substances having in their compositions only one reducible atomic group or bond, is often accompanied by the formation of several diffusion waves [1]. The appearance of two or more diffusion waves during the reduction of such organic molecules has different origins [2-4]. It was found that when reduction proceeds in buffer solutions having different pH values, the reduction potentials of the individual diffusion waves of different forms vary as the pH changes.

In the present work we investigated the reduction of m-nitrobenzenesulfonic acid, which has recently found wide use for the synthesis of valuable medicinal preparations, for the purpose of establishing the relationship of the nature of the reduction on the pH, and of finding suitable conditions for the quantitative determination of this compound.

EXPERIMENTAL

We studied the reduction of m-nitrobenzenesulfonic acid at the dropping mercury cathode in a concentration range from $0.4 \cdot 10^{-3}$ to $1.18 \cdot 10^{-3}$ M in buffer solutions having pH values from 2.03 to 13.0. For each buffer solution, several polarization curves were obtained, depending on the concentration of the m-acid used. Several of the polarograms obtained are presented in Fig. 1.

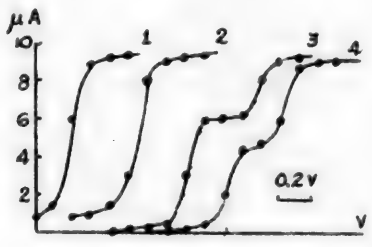

Fig. 1. Polarograms of m-nitrobenzenesulfonic acid, taken in solutions having different pH values (sensitivity 1:100, concentration of acid, $0.8 \cdot 10^{-3}$ M). 1) pH 2.03; 2) pH 6.24; 3) pH 8.7; 4) pH 9.7. Beginning of curves, 0.2 V.

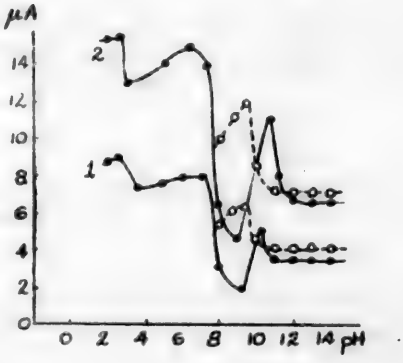

Fig. 2. Relationship of the diffusion current to the pH values for different concentrations of m-nitrobenzenesulfonic acid. The continuous line is for the first waves, the broken line is for the second waves. 1) Concentration $8 \cdot 10^{-4}$ M; 2) concentration $14.8 \cdot 10^{-4}$ M.

To plot the polarograms, we used a dropping mercury electrode of the usual construction, and a visual polarograph from the Gorky Scientific-Research Institute of Chemistry; the polarograph had a galvanometer with a maximum sensitivity of $0.55 \cdot 10^{-9}$ A per 1 mm of scale reading. We used a capillary having the following characteristics: the dropping period was 2.8 sec., and the volume of mercury flowing out per 1 second was 1.43 mg. All the measurements were carried out in a thermostat at a temperature of $20 \pm 0.5°$ C. As the anode, we used a saturated calomel electrode, the potential of which was arbitrarily assumed to be zero. In order to remove dissolved oxygen, hydrogen was blown through the solutions before polarographing.

As the standard solution of m-nitrobenzenesulfonic acid, we used a solution of its potassium salt, which is easily obtained in the pure form. Buffer solutions, consisting of a mixture of phosphoric, acetic and boric acids and potassium hydroxide, served as the indifferent electrolytes.

The experimental data obtained showed that the reduction of m-nitrobenzenesulfonic acid takes place at different half-wave potentials, depending on the pH values of the solutions.

In solutions having acid to weakly alkaline (pH 8.0) reactions, reduction was accompanied by the development of one diffusion wave on the polarogram. For solutions in which the pH values increased from 8.0 to 12.0, there were two diffusion waves. On further increases of the alkalinity of the solutions, the polarograms had only one diffusion wave.

In solutions in which two diffusion waves developed as a result of the reduction, the ratio of the diffusion currents did not remain constant. The height of the second diffusion wave in solutions having pH values from 8.0 to 9.4, amounted to one-third of the total wave height, but in buffer solutions having pH values from 9.7 to 12.0 it amounted to half of the total wave height.

A linear relationship between the diffusion current values and the concentrations of the sulfonic derivative being reduced was observed for all the buffer solutions studied. This relationship may be represented in the form of the equation $i_d = Kc$, where i_d is the diffusion current (in μA) and c is the concentration (in moles).

The value of the proportionality coefficient, K, differed for different buffer solutions, and amounted to approximately $10 \cdot 10^4$ μA/mole/liter. Some of the fluctuations of the proportionality coefficient values in the equation cited above depended on the relationship of the diffusion current values of the nitro-derivative being reduced to the pH values of the solution; this relationship is illustrated in Fig. 2. In slightly acid and neutral solutions, the diffusion current values pass through a minimum, occurring at a pH of approximately 4.0. In the region of weakly alkaline solutions, the relationship of the diffusion current to pH values again has a rather complex character. The diffusion current of the first wave passes through a minimum at a pH value of about 9.0, while the diffusion current of the second wave proceeds through a maximum. The maximum value of the diffusion current of the first wave occurs at the somewhat large pH value of 10.0.

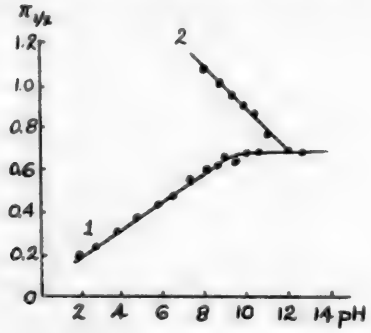

Fig. 3. Relationship of the half-wave potential of m-nitrobenzenesulfonic acid to the pH. 1) First wave; 2) second wave.

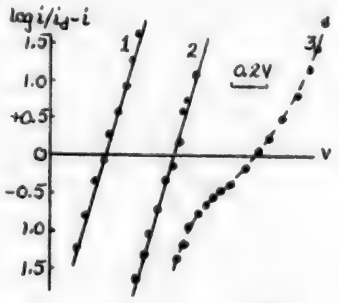

Fig. 4. Relationship between the potential and $\log \frac{i}{i_d - i}$ for solutions having different pH values. Concentration of m-nitrobenzenesulfonic acid $1.8 \cdot 10^{-3}$ M. 1) pH 2.6; 2) pH 9.7 (for first wave); 3) pH 9.7 (for second wave).

The complex character of the relationship of the diffusion current values to the hydrogen ion concentrations in the solutions indicated the presence of adsorption phenomena.

The half-wave potential of the reduction, like the diffusion current, depended on the concentration of hydrogen ions in the solutions. In acidic, neutral and slightly alkaline solutions, approximately up to a pH value of 8.5-9.0, the half-wave potential of the first reduction wave increased linearly with an increase of pH. The half-wave potential function of the reduction for these solutions may be represented by the equation:

$$\pi_{1/2} = -0.05 - 0.068 \text{ pH}.$$

In more alkaline solutions, beginning at a pH of approximately 10.0, the half-wave potential of the first diffusion wave remained unchanged. With an increase of the alkalinity of the solution, the half-wave potential of the second diffusion wave, appearing in solutions having a pH > 8.0, was displaced toward more positive values. The relationship of the half-wave potential of the second wave of m-nitrobenzenesulfonic acid to the pH value may be represented by the equation:

$$\pi_{1/2} = -1.88 + 0.1\ \text{pH}.$$

This relationship is represented graphically in Fig. 3. Since the half-wave potential of the second wave is displaced toward the region of more positive values, with an increase of the pH of the solution, an approach and merging of the individual waves occurs.

Analysis of the individual polarograms showed that, for diffusion waves having the least half-wave potentials, for all the acid concentrations and different pH values studied, the linear relationship between the half-wave potential and the quantity $\log \frac{i}{i_d - i}$ was maintained in accordance with the Heyrovsky-Ilkovic equation:

$$\pi = \pi_{1/2} - \frac{0.058}{n} \log \frac{i}{i_d - i},$$

in which $\pi_{1/2}$ denotes the half-wave potential and i_d is the limiting diffusion current.

For the second diffusion wave, at more negative potentials, the Heyrovsky-Ilkovic equation does not hold completely. The experimental values of the current (Fig. 4, 3) show considerable deviations from linearity.

From the value of the tangent of the angle formed by the line with the coordinate axis, it is possible to find the value of the quantity n, representing the number of electrons taking part in the electrode reaction. For the first diffusion wave this value was shown to be close to 1, but for the second, it was of the order of 0.4. It may be assumed that the reason for the non-observance of the Heyrovsky-Ilkovic equation is the irreversibility of the electrode reaction.

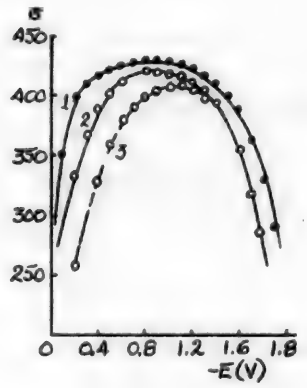

Fig. 5. Electrocapillary curve of mercury in the presence of a background I having a pH of 4.1, and m-nitrobenzenesulfonic acid (potential of the mercury estimated with reference to the sulfate-mercury electrode). 1) Background; 2) concentration of the acid $1.8 \cdot 10^{-4}$ M; 3) concentration of the acid $7.0 \cdot 10^{-3}$ M.

For the reduction of m-nitrobenzenesulfonic acid, the diffusion current depends on the reduction of the nitro-group, since the other atomic groups do not undergo reduction at the mercury dropping cathode. Related compounds not containing nitrogroups, and also m-nitrobenzenesulfonic acid, according to our data, do not belong to the reducible substances. At the same time, it is known from the large number of polarograms studied that the reduction of the nitro-group requires 6 electrons. Accordingly, it should be easy to find the value of the diffusion coefficient of m-nitrobenzenesulfonic acid, using the Ilkovic equation for the diffusion current:

$$i_d = 605 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C.$$

For buffer solutions having a pH of 2.0, calculation of the diffusion coefficient gave $0.4 \cdot 10^{-5}$ $cm^2 \cdot sec.^{-1}$, which agrees well enough with the diffusion coefficient values for similar organic molecules.

The experimental data presented show that the behavior of m-nitrobenzenesulfonic acid during reduction at the surface of a dropping mercury electrode depends essentially on the pH value of the indifferent electrolyte used as the background. It should be assumed that in acid solutions reduction is accompanied by the interaction of the hydrogen ions with the adsorbed m-acid molecules.

The electrocapillary curves (Fig. 5) showed that the adsorption of m-nitrobenzenesulfonic acid on the mercury surface was rather considerable. The form of the electrocapillary curves in the presence of a reducible substance differs substantially from the form of the electrocapillary curve of mercury in the presence of only a single background. There was an especially strong influence of the reducible substance in the ascending region of the electrocapillary curve at a not too negative electrode potential. All of the concentrations of m-nitrobenzenesulfonic acid studied had an influence on the form of the curve; the influence was greater, the larger the concentration of the m-acid. In the region of the more negative potentials, on the descending branch of the electrocapillary curve, the effect of the reducible substance was less substantial and did not always depend on the concentration of the m-acid.

In solutions having pH values greater than 8.0-9.0, reduction of the anion of m-nitrobenzenesulfonic acid proceeds at potentials which are more negative than the reduction potential of the acid molecule itself.

The capacity of m-nitrobenzenesulfonic acid to be reduced at the dropping mercury cathode may be utilized for the polarographic quantitative determination of this compound in m-aminobenzenesulfonic acid. For the

purpose of the determination, the most favorable background is a solution of potassium hydroxide, in which the amino- and nitro-acids are adequately dissolved. If a 5% solution of KOH is used, the diffusion wave of the reduction is observed at a potential of about -0.8 - -0.9 V. Under these conditions the amino-acid gives no diffusion wave and the determination is not impeded, since the amino-acid exerts no influence on the current strength and the half-wave potential of the m-nitro acid.

For the quantitative determination it was preferable to use a calibration curve, which was constructed by using a series of standard solutions containing known amounts of m-benzenesulfonic acid. Before polarographing, hydrogen was blown through the solutions for 15-20 minutes in order to remove dissolved oxygen. Under the conditions described, the accuracy of the determinations was of the order of 5%.

SUMMARY

1. The reduction of m-nitrobenzenesulfonic acid in solutions containing different concentrations of hydrogen ion was studied. It was shown that m-nitrobenzenesulfonic acid, at a given pH value of the background, was reduced in two waves.

2. For the reduction of m-nitrobenzenesulfonic acid, the relationship of the half-wave potential and the diffusion current to the pH value of the background solution was established.

3. The conditions for the quantitative determination of m-nitrobenzenesulfonic acid were determined.

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INVESTIGATION OF THE REACTION OF UREA WITH PHENOL BY METHODS OF PHYSICO-CHEMICAL ANALYSIS. V.

N. Z. Rudenko and D. E. Dionisyev

Continuing our work on the study of the reaction of urea with phenol by the methods of physico-chemical analysis, we attempted to explain how the introduction of a methyl group into the phenol molecule and condensation with a second aromatic nucleus would affect the reaction with urea. For this purpose, we studied binary systems formed from urea and α-naphthol, β-naphthol and m-cresol. The fusibility, density, viscosity and electrical conductivity of the systems were investigated.

The experimental methods were as described earlier [1], and the measurements were carried out in the liquid phase at three temperatures. The concentrations were expressed in mole per cents, and the viscosity in centipoises.

System urea–α-naphthol. The fusibility of this system was studied by Puschin and König [2]. The fusibility curve, with a simple eutectic, enabled them to conclude that chemical interaction was absent from the system. We repeated the fusibility investigation, and also studied the density, viscosity and electrical conductivity at 130, 140 and 150°.

For the work we used urea which, after repeated recrystallization from water, had m.p. 132.7°. The α-naphthol, after recrystallization from benzene, had m.p. 96°.

Since our data on fusibility were always close to the data of Puschin and König, we did not construct a fusibility curve.

The viscosity curves of the system are presented in Fig. 1. All three of the viscosity isotherms pass through maxima in the region of 75 mole % of urea. At increased temperatures, the maxima are shifted slightly toward the more viscous component.

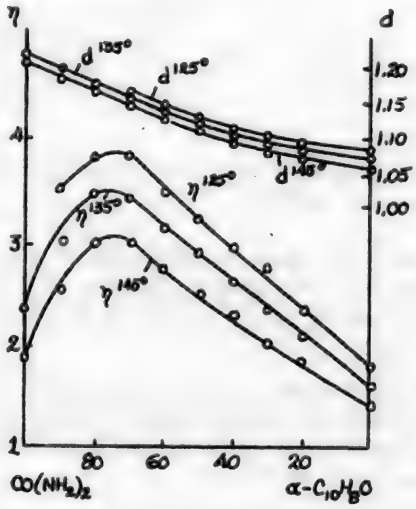

Fig. 1. Viscosity and density of the system urea–α-naphthol.

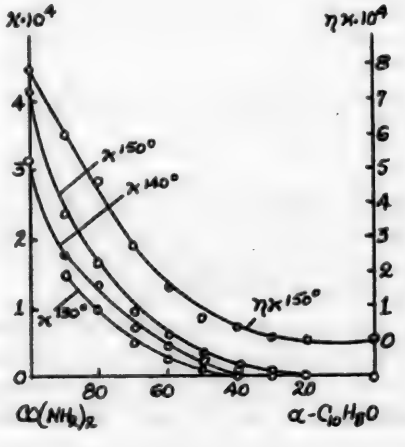

Fig. 2. Electrical conductivity, and electrical conductivity corrected for viscosity, of the system urea–α-naphthol.

The temperature coefficient of the viscosity also was at a maximum in the region corresponding to 75 mole % urea. In the same figure, density isotherms of the system are shown; they are slightly convex toward the composition axis.

Fig. 2 shows the isotherms of electrical conductivity which represent its monotonous decrease, and are convex toward the composition axis, without any unusual points.

The "correction" of the electrical conductivity values for viscosity ($\eta\kappa$) did not change the course of the curves, in spite of the presence of viscosity maxima. In Fig. 2 the "corrected" electrical conductivity isotherm is given for 150°, the other two isotherms having precisely the same course.

System urea–β-naphthol was studied for the first time by the methods of physico-chemical analysis. We studied its fusibility, and in the liquid phase we studied its density, viscosity and electrical conductivity at 125, 135 and 145° For the work we used β-naphthol which was repeatedly recrystallized from alcohol; its m.p. was 122.4°.

The fusibility curves of the system are presented in Fig. 3. The curves consist of three branches, two branches of crystallization of the pure components, and a branch of crystallization of the compound $2\beta\text{-}C_{10}H_7OH \cdot CO(NH_2)_2$, with m.p. 108°. The eutectic points at 105 and 104° have the compositions, 25 and 42.5 mole % urea.

In Fig. 4 are shown viscosity isotherms which, as in the preceding system, pass through maxima in the region of 75 mole % urea. The maxima are hardly shifted with a change of temperature. The temperature coefficient of the viscosity is also at a maximum in this region. The density isotherms (Fig. 4) are represented by curves which are slightly convex toward the composition axis.

The electrical conductivity isotherms (Fig. 5), both in form and in absolute values, were almost duplicates of the isotherms found for the system urea–α-naphthol.

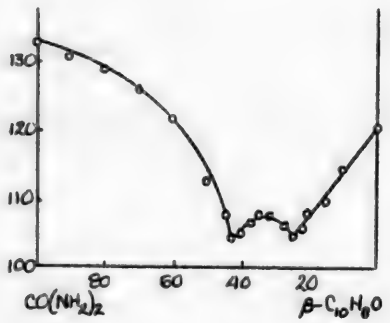

Fig. 3. Fusibility of the system urea–β-naphthol.

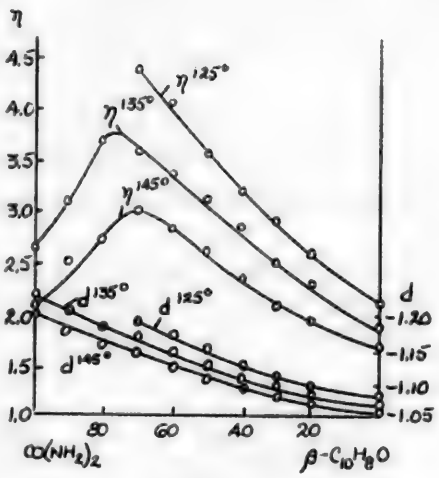

Fig. 4. Viscosity and density of the system urea–β-naphthol.

The electrical conductivities in these systems were determined by the comparatively large electrical conductivity of urea, which decreased in proportion to the increase in the amount of naphthol. The "correction" of the electrical conductivity for viscosity (Fig. 5), in spite of the presence of maxima on the viscosity curves, did not change the course of the isotherms.

System urea–m-cresol. The fusibility of the system was studied by Puschin and Sladovic [3]. They obtained curves from which they subjectively drew the conclusion that an incongruently melting compound of 1:1 composition formed in the system. The curves that we obtained were similar to those of the cited authors. It is risky to infer from them that chemical reaction occurs in the system.

An investigation of the liquid phase should give an indication of any chemical reaction in the system. We, therefore, investigated the density, viscosity and electrical conductivity at 120, 130 and 140°.

For the work, we used "c.p." grade m-cresol, purified it by distillation, and collected the fractions boiling at 202.6-202.8°, and having m.p. of 10.6° .

The viscosity isotherm for 140° consisted of an S-shaped curve having a slight inflexion. In proportion to the decrease of temperature, the isotherms straightened out, losing their S-shaped forms (Fig. 6).

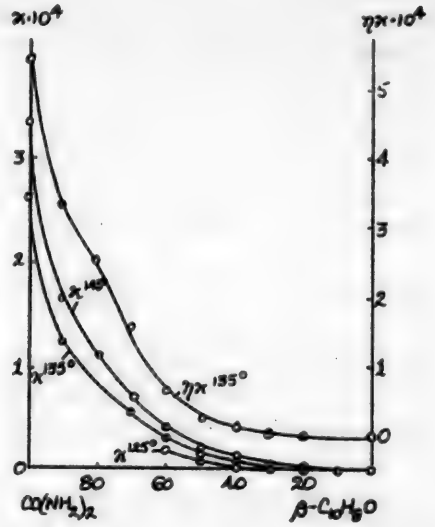

Fig. 5. Electrical conductivity, and electrical conductivity corrected for viscosity, for the system urea—β-naphthol.

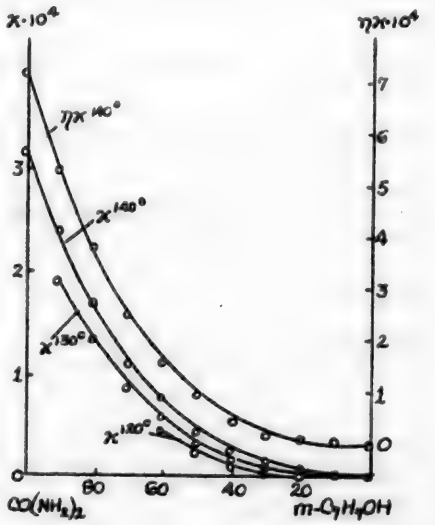

Fig. 7. Electrical conductivity, and electrical conductivity corrected for viscosity, of the system urea—m-cresol.

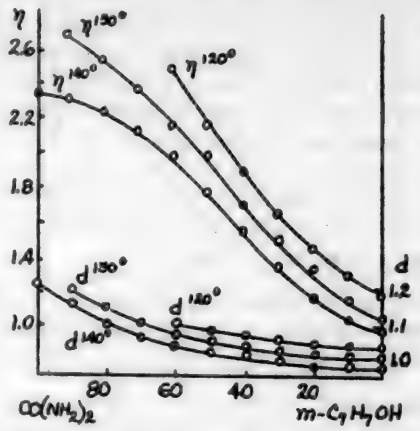

Fig. 6. Viscosity and density of the system urea—m-cresol.

The density curves (Fig. 6), like those in the preceding system, were convex toward the composition axis. The density decreased rather rapidly from the density of urea to that of a mixture with 60 mole % urea, and then decreased evenly.

The curves of the electrical conductivities $\varkappa$ and $\eta\varkappa$ (Fig. 7), of the system fall monotonously from the natural electrical conductivity of urea to that of m-cresol, and are convex toward the composition axis.

DISCUSSION OF RESULTS

It is known that the dissociation constants of α- and β-naphthol are larger than that of phenol. If this regularity also holds for the solvent, urea, then it can be expected that because of the large mobility of the hydrogen of the phenolic hydroxyl group in α- and β-naphthols, their reaction with urea will be more clearly expressed than with phenol. With urea, phenol forms the very unstable compound, $CO(NH_2)_2 \cdot 2C_6H_5OH$, which decomposes completely in the liquid phase [1]. Investigation of the system urea—α-naphthol showed that in it chemical reaction between the components occurs. This chemical reaction was reflected on the viscosity curves, which had clear maxima in the region of 75 mole % urea; it is true that it is difficult to judge the composition of the compound forming, from the form of this maximum, but it can be assumed that its composition is $2CO(NH_2)_2 \cdot C_{10}H_7OH$. This compound was not indicated by the fusibility curve. In the literature it is reported that a compound which is not observed by the fusibility method, may be reflected by the curves of properties in the liquid phase [4, 5]. The electrical conductivity curves, having uniform courses, did not reflect chemical reaction in the system. However, electrical conductivity curves of such form are known for systems in which chemical interaction occurs [6, 7].

In contrast to the system urea—α-naphthol, in the system urea—β-naphthol reaction between the components was also observed by the fusibility method. On the fusibility curve reflection of the considerably dissociated compound $CO(NH_2)_2 \cdot 2C_{10}H_7OH$ was found, and it corresponded to a maximum m.p. of 108°.

The curves of the properties studied in the liquid phase were very much like the corresponding curves in the preceding system. The viscosity isotherms passed through maxima in the region of 75 mole %, i.e., in the liquid phase a different compound from $CO(NH_2)_2 \cdot 2C_{10}H_7OH$ is reflected, which evidently is $2CO(NH_2)_2 \cdot C_{10}H_7OH$. The fact that in the liquid phase the compound $CO(NH_2)_2 \cdot 2C_{10}H_7OH$ dissociates completely, confirmed the assumption [8] made earlier that urea in such compounds is the donor of one electron pair, but that this electron pair is accepted by a dimer of the second component. In the liquid phase β-naphthol is found to be present as the monomer to a great extent, and this monomer reacts with urea. It should be pointed out that in reaction with urea, β-naphthol shows a greater activity than α-naphthol just as in systems with β-naphthylamine [9] and pyridine [10], which in all probability was caused by the larger dipole moment and the lesser spatial "inaccessibility" of the β-naphthol. In comparison with phenol, the condensed nucleus in the naphthols increases the tendency of the latter toward chemical reaction with urea.

It can be assumed that the presence of the methyl radical in the phenol nucleus (for cresol) will hardly increase the tendency of the latter toward chemical reaction with urea.

Investigation of the system, urea–m-cresol, showed that there is no basis for treating the fusibility curves as indicators of chemical reaction in the system. The isotherms of properties of the liquid phase also give no direct indication of the presence of chemical reaction. It is true that the viscosity curves at first glance may have S-shaped forms, which usually indicate chemical reaction in the system [11].

However, in the present case, the S-form of the curves decreases with a decrease of temperature. In our opinion, the appearance of such S-shapes of the isotherms at increased temperature was caused, on the one hand, by an increase of the dissociation of the associated molecules of m-cresol, and on the other, by the larger change of the viscosity for urea than for the subsequent mixture.

SUMMARY

1. The fusibility, viscosity, density and electrical conductivity of the systems urea–α-naphthol, urea–β-naphthol and urea–m-cresol were investigated.

2. The presence of chemical reaction in the system urea–α-naphthol, with formation, in all probability, of the compound $2CO(NH_2)_2 \cdot C_{10}H_7OH$, was established.

3. It was shown that in the system urea–β-naphthol two compounds form – $CO(NH_2)_2 \cdot 2C_{10}H_7OH$ and, probably, $2CO(NH_2)_2 \cdot C_{10}H_7OH$.

4. For the system urea–m-cresol no direct indication of chemical reaction between the components was obtained.

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*** See Consultants Bureau Translation, page 67.

**** See Consultants Bureau Translation, page 751.

CATALYTIC SYNTHESIS OF KETONES

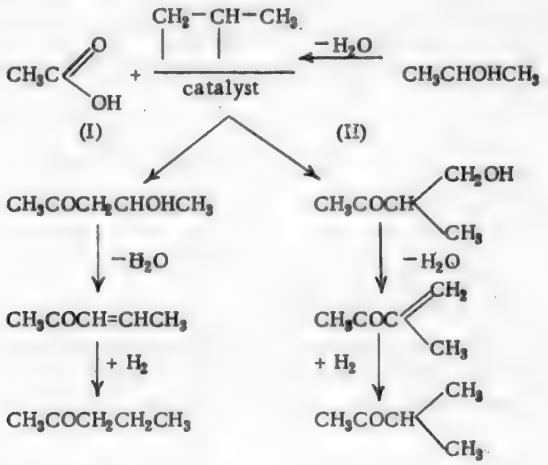
IV. SYNTHESIS OF METHYL PROPYL, METHYL ISOBUTYL, DIISOPROPYL AND ISOPROPYL BUTYL KETONES

I. P. Yakovlev

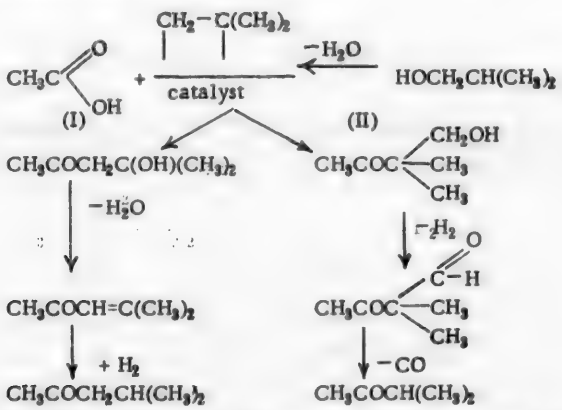
In a previous report [1] it was shown that ketones having the same total number of carbons as the initial product are formed by reaction of acids and acid anhydrides with aliphatic alcohols over chrome-manganese catalysts [2]. Mixtures of acid chlorides and alkyl halides [3] undergo similar transformations. It was postulated that the functional group connected to the carbonyl group of the acid migrates to a new bond position which forms in the second component participating in the ketonization reaction.

Further verification of the reaction scheme proposed previously for the catalytic ketonization, is presented in the present work. Acetic acid and isopropyl and isobutyl alcohols were used as the starting materials. It might be assumed that the reaction proceeds according to an analogous scheme.

1. For isopropyl alcohol and acetic acid:



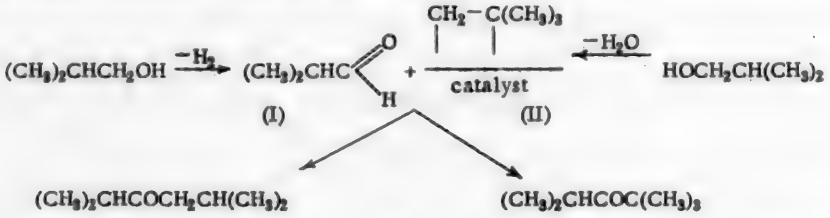
2. For isobutyl alcohol and acetic acid:



According to the second direction of the reaction, we would expect the formation of a keto alcohol, but this keto alcohol would be easily converted to the keto aldehyde, and the latter, losing carbon monoxide, would be converted to methyl isopropyl ketone.

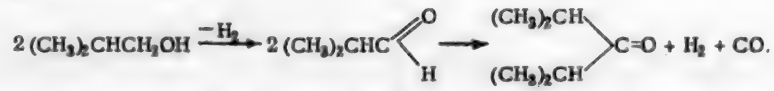
The experimental examination actually confirmed the proposed hypothesis. From a mixture of acetic acid and isopropyl alcohol in the presence of hydrogen, the two expected ketones – methyl n-propyl ketone and methyl isopropyl ketone – were formed. True, the yields of the ketones were negligible, since isopropyl alcohol is readily converted to acetone by the catalyst used. If the reaction is carried out in the absence of hydrogen, then according to the scheme, two unsaturated ketones, methyl isopropenyl ketone and methyl propenyl ketone, should form. Of these two ketones, only methyl propenyl ketone was formed. The presence of only one unsaturated ketone is understandable, if we consider the properties of these substances: while methyl propenyl ketone is a sufficiently stable ketone, distilling without polymerization, methyl isopropenyl ketone, on the other hand, is unstable; it polymerizes readily, even during ordinary storage. Under the conditions of formation of these ketones, methyl isopropenyl ketone is easily polymerized, and is hardly observed in the catalysis products, whereas the other ketone is produced at high temperature ranges (up to 8% of the theoretical amount), and may be separated from the catalyst. (It is known [4] that the yield of methyl vinyl ketone from acetic acid and ethyl alcohol amounts to less than 1%.)

For isobutyl alcohol and acetic acid, proceeding from the scheme, the formation of methyl isobutyl ketone and methyl isopropyl ketone would be expected. The formation of methyl isobutenyl ketone in the absence of hydrogen should proceed in small yields, since the alcohol, being dehydrogenated, yields hydrogen to the system, and this hydrogen hydrogenates the unsaturated ketone; therefore, experiments were not carried out without the addition of hydrogen to the system during ketonization. In experiments carried out in the presence of hydrogen, both of the proposed saturated ketones were produced, i.e., the ketonization scheme was shown to be valid. However, together with methyl isobutyl ketone and methyl isopropyl ketone, three more ketones were obtained: diisopropyl ketone, isopropyl isobutyl ketone and isopropyl tert-butyl ketone. It might be assumed that the formation of these ketones proceeded because of the isobutyl alcohol. In order to verify this assumption, an experiment for the ketonization of isobutyl alcohol was conducted. Proceeding from the proposed scheme, the formation of isopropyl isobutyl ketone and isopropyl tert-butyl ketone may be represented as follows:

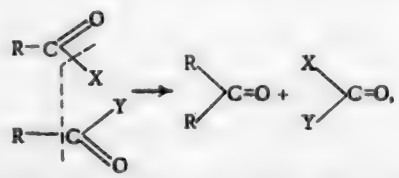


The experiment was carried out in the absence of hydrogen, since hydrogen is not required according to the scheme for the ketonization reaction – one alcohol molecule is dehydrated, the other is dehydrogenated, and the subsequent reaction of the products with the hydrogen displaced from the aldehyde group, leads to the formation of the two ketones.

As to the formation of diisopropyl ketone, this ketone was formed according to an entirely different scheme – according to the scheme of ketonization of an acid:



For the latter reaction it was thought that both the acid and the aldehyde and their mixture should follow the general scheme of decomposition during catalytic ketonization. In general form this scheme might be represented as:



where X and Y might be: H, OH, halogen, OR, OCOR, etc., and R might be alkyl or hydrogen. In order to verify this assumption, experiments on the ketonization of the corresponding derivatives and their mixtures were carried out. The experimental results confirmed the hypothesis.

EXPERIMENTAL

Initial reactants. Acetic acid, b.p. 118°, n_D^{25} 1.369; isopropyl alcohol, b.p. 82-83°, n_D^{20} 1.377; isobutyl alcohol, b.p. 107°, n_D^{25} 1.397. Hydrogen was obtained by the action of dilute H_2SO_4 on granulated zinc, not containing aresnic, and was purified by a chromic mixture.

Procedure. A chrome-manganese catalyst was placed in the usual catalytic apparatus in the zone of comparatively uniform heating. After 2-3 experiments, the catalyst was regenerated by calcination in a porcelain dish over a flame jet. The condensates obtained, depending on the quantity of water and original alcohol in them, were treated somewhat differently. The acid residue, which did not enter into reaction, was extracted with soda, the alcohol – with calcium chloride. Then the dry catalyzate was carefully fractionated.

Depending on the experiment, in some cases hydrogen was introduced into the system in equimolecular quantities.

1. Synthesis of methyl propyl and methyl isopropyl ketones. a) Experiment without hydrogen. Isopropyl alcohol and acetic acid in a volume ratio of 1:3 were passed over the chrome-manganese catalyst in a quantity of 80 ml at 400, 430 and 460° at rates of 13, 20 and 40 ml/hour. Acetone was the chief product of the ketonization of acetic acid and isopropyl alcohol in the absence of hydrogen. In all the experiments, except that carried out at 460°, the condensate contained the initial alcohol which had not entered into reaction.

On passing 120 ml of the initial mixture at 400°, 35 g of catalyzate was obtained. The following fractions were obtained by distillation: 1st 56-58°, 10.3 g; 2nd 58-65°, 8 g; 3rd, 66-79°, 3 g; and 4th, 81-83°, 2 g.

The 1st fraction was pure acetone: b.p. 56°, $n_D^{19.5}$ 1.3589; the 2,4-dinitrophenylhydrazone had m.p. 126°. The 2nd fraction consisted chiefly of acetone with negligible amounts of the substance of the 3rd fraction. The 4th fraction consisted of the original isopropyl alcohol. The higher ketones were not observed.

At 430°, and a feed rate of 20 ml/hour, from a 90 ml mixture 25 ml of catalyzate was obtained. On distillation, we obtained the same fractions and a fraction at 92-96°, 0.26 g, which proved to be methyl isopropyl ketone: $n_D^{19.6}$ 1.3869, 2,4-dinitrophenylhydrazone m.p. 119°.

Finally, 50 ml of isopropyl alcohol and 150 ml of acetic acid were taken and passed at a rate of 40 ml/hour at 460°. 84 ml of catalyzate was obtained. The catalyzate was treated with soda and calcium chloride. Acetone was removed by boiling on a water bath. The residue distilled from a Favorsky flask. The following fractions were obtained: 1st, 90-98°, 2.1 g; 2nd, 98-110°, 0.4 g; 3rd, 120-131°, 4.2 g; and 4th, 131-140°, 0.4 g. The 3rd and 4th fractions were combined and distilled again. The main volume came over at 122-124° (3.9 g). This was methyl propenyl ketone: n_D^{19} 1.4342, d_4^{19} 0.8629, MR_D 25.36, calculated, 24.83; the 2,4-dinitrophenylhydrazone had m.p. 205-208°. The ketone was oxidized in a neutral medium by potassium permanganate. For 1.5 g of the ketone, 4.8 g of $KMnO_4$ was used. It might be assumed that the oxidation proceeded in one of three directions.

$$C_5H_8O \xrightarrow{1} 2\,CH_3COOH + HCOOH$$
$$C_5H_8O \xrightarrow{2} CH_3COOH + (COOH)_2 + HCOOH$$
$$C_5H_8O \xrightarrow{3} CH_3COCOOH + CH_3COOH$$

Each of these reactions requires 1.43, 2.14 and 1.15 g of oxygen, respectively, for 1.5 g of the ketone. 1.16 g of oxygen was consumed. From the filtrate containing the oxidation products, a voluminous yellow precipitate (0.5 g) was obtained with 2,4-dinitrophenylhydrazine, and after recrystallization from acetic acid it melted at 118°, which corresponded to the melting point of the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone; the sample when mixed with the known substance caused no m.p. depression. The presence of methyl isopropyl ketone was connected with the insufficiently pure 122-124° fraction. Acetic acid, giving the acetanilide, with m.p. 112°, with aniline (the mixed sample gave no m.p. depression), was isolated, and formic acid (by a voluminous mercurous chloride precipitate) was observed. The acetic and formic acids, distilled together, were neutralized with alkali to a phenolphthalein end point, consuming 0.78 g of NaOH. Neither oxalic nor pyruvic acids were separated. Thus, it can be assumed that oxidation proceeded according to the first scheme.

b) The reaction with hydrogen was carried out under the conditions described above. On passing 60 ml of the initial mixture at 400°, 45 g of condensate was obtained. After treatment and distillation, this condensate was separated into the following fractions: 1st, 56-58°, 10 g; 2nd, 58-65°, 17.4 g; 3rd, 65-83°, 3 g; 4th, 92-96°, 0.4 g; and 5th, 98-104°; 0.2 g. At 430 and 460° the composition of the fractions was the same as at 400°, but the amounts of ketones forming were different in each case. Since the 4th and 5th fractions were of greatest interest, i.e., were

the ones containing methyl propyl ketone and methyl isopropyl ketone, their yields (in %) based on isopropyl alcohol used, are given below.

Temperature of experiment	$CH_3COCH_2CH_2CH_3$	$CH_3COCH(CH_3)_2$
400°	0.3	0.6
430	0.6	1.5
460	1.3	8.2

Methyl isopropyl ketone, b.p. 95-96°, n_D^{19} 1.3869, d_4^{19} 0.7987, MR_D 25.34, calculated 25.30; 2,4-dinitrophenylhydrazone, m.p. 118-119°, no depression in a mixed sample with the 2,4-dinitrophenylhydrazone of this ketone obtained starting from the acid.

Methyl propyl ketone, b.p. 102-103°, n_D^{19} 1.3900, d_4^{19} 0.8118, MR_D 25.12, calculated 25.30; the 2,4-dinitrophenylhydrazone, m.p. 142-143°, gave no depression with the 2,4-dinitrophenyldrazone of this ketone obtained from acetic and butyric acids.

2. Synthesis of ketones from a mixture of acetic acid and isobutyl alcohol. 3 moles of acetic acid and 1 mole of isobutyl alcohol were used in the reaction. The mixture was passed at a rate of 15 ml/hour over a chrome manganese catalyst applied to an asbestos mat, at 450° in the presence of H_2 (100 ml/min). Yield, 170 ml catalyzate: the lower aqueous layer was separated, and the upper layer treated with dry $CaCl_2$, distilled from a Würtz flask and fractionally distilled. [illegible]n. After the first fractionation, the following fractions were separated: 1st, 58°, 20 ml; 2nd, 58-94°, 4 ml; 3rd 94-101°, 14.2 ml; 4th, 101-107°, 10.1 ml; 5th, 107-123°, 17.5 ml; 6th, 123-134°, 4.3 ml; 7th, 134-144°, 2 ml; and 8th, 144-155°, 2.8 ml. The experiment was repeated for the purpose of accumulating the fractions obtained. These fractions, combined with the preceding fractions, were repeatedly fractionated and studied. It was shown that the 1st fraction was acetone; the 2,4-dinitrophenylhydrazone, having a m.p. of 126°, when mixed with the known substance gave no depression; the 2nd fraction was methyl isopropyl ketone, m.p. 94-96°, n_D^{22} 1.3874, d_4^{22} 0.8001, MR_D 25.14, calculated 25.30; the 2,4-dinitrophenylhydrazone had m.p. of 118°; no depression when mixed with the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone obtained from acetic acid and isobutyl alcohol. From the 101-123° fraction, the following were separated: a) original isobutyl alcohol and b) methyl isobutyl ketone, b.p. 116-118°, n_D^{20} 1.3990, d_4^{20} 0.8106, MR_D 29.84, calculated 29.92; the 2,4-dinitrophenylhydrazone had m.p. 92-94°; the semicarbazone had m.p. 131°; the semicarbazone when mixed with the known substance produced no depression. (The known ketone was prepared starting from the acid.) From the 4th fraction, diisopropyl ketone was separated, b.p. 124-127°, $n_D^{24.5}$ 1.3965, $d_4^{24.5}$ 0.7972, MR_D 34.40, calculated 34.54; the 2,4-dinitrophenylhydrazone had m.p. 90-91°; the sample when mixed with the 2,4-dinitrophenylhydrazone of the known ketone obtained from isobutyl alcohol, and also from the pure isobutyl aldehyde and, finally, from isobutyric acid, produced no depression. From the 7th fraction, isopropyl tert-butyl ketone was separated, b.p. 134-136°, n_D^{24} 1.4020, d_4^{24} 0.8042, MR_D 38.92, calculated 39.15; the 2,4-dinitrophenylhydrazone melted at 87-89°. From the 8th fraction, isopropyl isobutyl ketone with a b.p. of 144-148°, n_D^{24} 1.4050, d_4^{24} 0.8110, MR_D 38.69, calculated 39.15, was separated; the 2,4-dinitrophenylhydrazone had m.p. 113°. This 2,4-dinitrophenylhydrazone was also tested by the method of mixing a sample with the 2,4-dinitrophenylhydrazone of the ketone obtained from one alcohol.

3. Synthesis of ketones from isobutyl alcohol. 175 ml of isobutyl alcohol was passed over a chrome-manganese catalyst (80 ml) at 460° at a rate of 15 ml/hour. Simultaneously, hydrogen was supplied at a rate of 30 ml/min. (On repetition of the experiment, no additional hydrogen was introduced into the system, and the results were the same.) 107 ml of a catalyzate having a cinnamon color was obtained. The catalyzate was dried with anhydrous sodium sulfate, distilled and fractionated; thus, 49 ml of isobutyraldehyde, with b.p. of 64-68°, was obtained; 14.5 ml of isobutyl alcohol did not enter into reaction. In addition, the following ketones were obtained: 1) Diisopropyl ketone, 3.1 ml, b.p. 124-126°, n_D^{24} 1.3955, d_4^{24} 0.7991, MR_D 34.24, calculated 34.54; the 2,4-dinitrophenylhydrazone had m.p. 90-91°; no m.p. depression in mixed sample. 2) Isopropyl tert-butyl ketone, 4.6 ml, b.p. 133-136°, n_D^{24} 1.4035, d_4^{24} 0.8041, MR_D 38.89, calculated 39.15; the 2,4-dinitrophenylhydrazone had m.p. 88-89°. 3) Isopropyl isobutyl ketone, 6.2 ml, m.p. 144-148°, n_D^{24} 1.4080, d_4^{24} 0.8115, MR_D 38.91, calculated 39.15; the 2,4-dinitrophenylhydrazone had a m.p. of 112-113°.

Moreover, from the residue left after the distillation, a fraction with b.p. 175-185° (about 2 ml), n_4^{24} 1.4600 was separated, but we were unable to identify it, since the product of its reaction with 2,4-dinitrophenylhydrazine melted in a wide range. Apparently, this fraction contained the products of the secondary condensation of the ketones and aldehydes, forming both in the catalytic tube, and during the fractionation of the catalyzate.

SUMMARY

1. On the basis of acetic acid and isopropyl alcohol, and acetic acid and isobutyl alcohol as examples, a proposed scheme of ketonization has been verified.

2. The synthesis of ketones from carbonyl-containing compounds proceeded according to the general type of ketonization of acids. Hence, two essentially different mechanisms of the formation of ketones were established, each of which has its specificity and points in common.

3. It was found that with a chrome-manganese catalyst, from mixtures of acetic acid and isopropyl alcohol, and acetic acid and isobutyl alcohol, the expected ketones were formed, but in small yields, and the mixture of ketones formed was difficult to separate into individual components. However, this method may be used under laboratory conditions.

4. In order to shift the reaction toward the formation of a particular ketone, it is necessary to use a selective catalyst.

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* See Consultants Bureau Translation, page 143.

REACTIONS OF DIKETENE

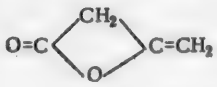
III. REACTION OF DIKETENE WITH SOME AROMATIC HYDROXY COMPOUNDS. SYNTHESIS OF ACETOACETYLPHENOLS

K. B. Rall and V. V. Perekalin

In the present work the almost univestigated reactions of diketene with phenols [1, 2] were studied for the following purposes: 1) development of a method for obtaining esters of aromatic hydroxy compounds and acetoacetic acid, which are not obtained by reaction of phenols with ethyl acetoacetate; 2) investigation of the chemical transformations of acetoacetyl derivatives, particularly the feasibility of their transformation to compounds of the methylcoumarin series, usually synthesized from aromatic hydroxy compounds and ethyl acetoacetate; 3) elucidation of the mechanism of the reaction of diketene with aromatic hydroxy compounds.

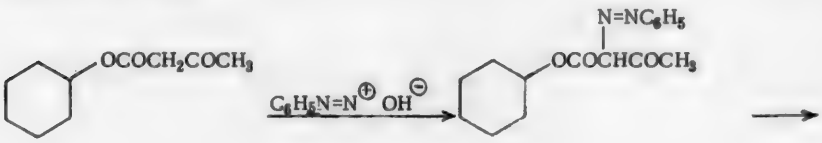
The acetoacetic esters of the aromatic hydroxy compounds may be used as plasticizers and solvents for varnishes. Among the coumarin derivatives, diverse physiologically active substances occur: analogs of the vitamins of the P [3] and K [4] groups, inactivators of vitamin K [5], insecticides [6] and herbicides [7].

The problem of the structure of diketene was not completely solved for a long time. The most recent investigations apparently enable us to assume that diketene is the β-lactone of 3-hydroxybutenoic acid [8-10].

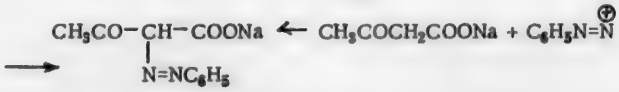


The reaction of diketene with phenol ($K_{OH} = 1.2 \cdot 10^{-10}$)* has been studied under various conditions (in media of different solvents and without them, in the absence of and with the participation of catalysts). In a benzene medium in the presence of pyridine, and in ether in the presence of concentrated sulfuric acid, acetoacetylphenol (I) forms. With the establishment of the structure of the acetoacetylphenol and all the acetoacetyl derivatives obtained for the first time, one can take advantage of their capacity for entering into azo-coupling reactions because of the methylene group of the acetoacetyl radical, and also their capacity for hydrolysis, with the formation of acetone and the original hydroxy compound.

By azo-coupling of acetoacetylphenol with diazobenzene, benzeneazoacetoacetylphenol (II) was obtained; its structure was verified by hydrolysis, which led to the formation of benzeneazoacetoacetic acid, described in the literature, and identified by the product specially synthesized from ethyl acetoacetate and diazobenzene. The azo dyes cannot have a different structure, since the diazo-compounds do not enter into the nucleus of the acyl derivatives of phenol.

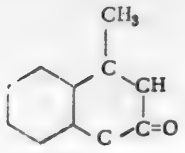


(I) (II)



During the investigation of the chemical transformation of acetoacetylphenol, only in concentrated sulfuric acid did we succeed in obtaining 4-methylcoumarin (III) in a small yield.

* K_{OH} equals the acidity constant.



(III)

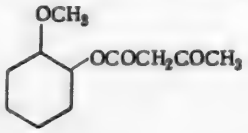
The structure of 4-methylcoumarin, like all the other coumarin derivatives that we synthesized, was established by matching spectral absorption curves and melting points, and by the absence of melting point depressions on mixing the sample with the known corresponding coumarin obtained, as is well-known, from ethyl acetoacetate.

The reactions of diketene with the ortho- and para-derivatives of phenol, containing electropositive and electronegative substituents, were studied further.

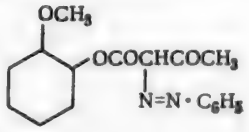
A study of the reactions of diketene with diatomic phenols (pyrocatechol and hydroquinone) showed that they belong to diketene reactions of a different type.

Pyrocatechol, like the majority of ortho-substituted compounds, did not enter into reaction with it. However, the replacement of a hydrogen atom of one of the hydroxyl groups in pyrocatechol changed the picture sharply; guaiacol formed acetoacetylguaiacol (IV) with diketene in the presence of basic (pyridine) and acidic (concentrated sulfuric acid) catalysts.

The structure of the acetoacetylguaiacol was established by the azo-coupling reaction which led to the formation of benzeneazoacetoacetylguaiacol (V). The diazo-compound could not enter into the nucleus, since neither anisol nor its ortho-substituted product could undergo the azo-coupling reaction.

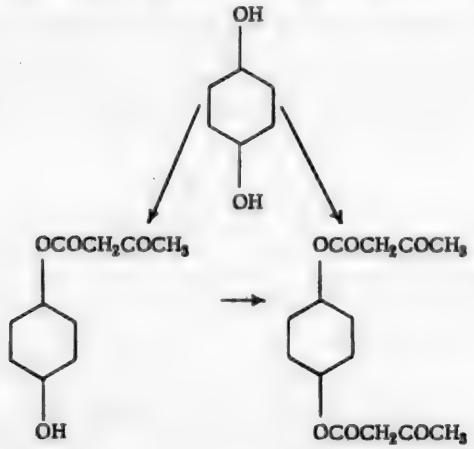


(IV)



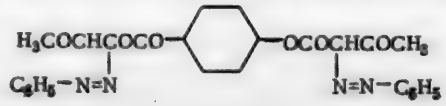
(V)

Hydroquinone ($K_{OH} = 5.7 \cdot 10^{-11}$) readily formed monoacetoacetylhydroquinone (VI) and diacetoacetylhydroquinone (VII). The latter is also formed by the reaction of the monoacetyl derivative with diketene.



(VI) (VII)

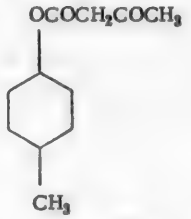
The reaction proceeds only in the presence of pyridine. In order to verify its structure, disbenzeneazodiacetoacetylhydroquinone (VIII) was obtained from diacetoacetylhydroquinone and diazobenzene.



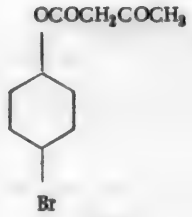
(VIII)

At attempt to carry out a transformation of acetoacetylhydroquinone to the coumarin derivative failed. Apparently, this is accounted for by its ease of hydrolysis, which proceeds even in alcohol solution in the cold.

o-Cresol ($K_{OH} = 6.3 \cdot 10^{-11}$) and o-bromophenol, in spite of a wide variation of conditions, did not react with diketene. p-Cresol ($K_{OH} = 6.7 \cdot 10^{-11}$) and p-bromophenol, in the presence of pyridine, formed the corresponding acetoacetyl derivatives (IX, X):



(IX)



(X)

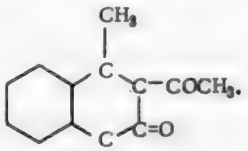
Numerous attempts to bring salicylic acid and its methyl and phenyl esters into this reaction were not successful.

Somewhat unexpectedly it was shown that p-hydroxybenzoic acid did not react with diketene; its ($K_{OH} = 5.8 \cdot 10^{-10}$ value was close to the value of the acidity constant for phenol ($K_{OH} = 1.2 \cdot 10^{-10}$), but the carboxyl group was spatially removed from the hydroxyl.

Ortho- and para-nitrophenols ($K_{OH} = 6.8 \cdot 10^{-8}$ and $7 \cdot 10^{-8}$, respectively) did not react with diketene.

Salicylaldehyde ($K_{OH} = 10^{-8}$) differed sharply from ortho-substituted phenol with respect to diketene, and particularly, its K_{OH} value was close to that of o-nitrophenol. In a solution of benzene in the presence of pyridine or potassium acetate, it formed 3-acetyl-4-methylcoumarin (XI) in yields of 40 and 80%, respectively; without a catalyst, the yield was small, and was equal to 4.5%.

In order to elucidate the course of the reaction, the aldehyde group was shielded by formation of azomethine, which was reacted with diketene, and also formed the product (XI).



(XI)

Benzaldehyde in benzene, in the presence of pyridine, did not react with diketene, but under the influence of potassium acetate, benzylideneacetone was formed. Benzaldehyde did not react with ethyl acetoacetate. Hence, the nature of the reaction of diketene with salicylaldehyde was determined by the specific positions of the hydroxyl and aldehyde groups.

p-Hydroxybenzaldehyde ($K_{OH} = 2.2 \cdot 10^{-8}$), like nitrophenol, did not react with diketene, apparently because of the high acidity constant.

The capacity of para-substituted phenols to form acetoacetyl derivatives with diketene is determined by the hydroxyl acidity constant (10^{-10}—10^{-11}). The ortho-derivatives usually do not react with diketene (except salicylaldehyde and guaiacol), apparently because of the blocking action of the substituents on hydroquinone.

EXPERIMENTAL

1. Acetoacetylphenol (I). a) 4.7 g phenol was dissolved in 30 ml of benzene, several drops of pyridine were added and, over a period of 10 minutes, 4.5 g diketene was added dropwise at −10°. The mixture was boiled for 1.5 hours. After removal of the benzene, the remaining mass crystallized.

The white crystals had m.p. of 50° (from concentrated alcohol solution); they were soluble in benzene, xylene, chlorobenzene, and methyl alcohol; the yield was 6.36 g (72.3%).

0.1200 g sub.: 0.2960 g CO_2; 0.0641 g H_2O. 0.1024 g sub.: 0.2525 g CO_2; 0.0514 g H_2O. 0.0998 g sub.: 5.52 g C_3H_6O; Δt 0.16°. 0.1064 g sub.: 5.564 g C_3H_6O; Δt 0.17°. Found %: C 67.30, 67.30; H 5.94, 5.62. M 188.7; 187.8. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.65. M 178.18.

b) To a solution of 14 g (0.16 mole) phenol in 25 ml ether, at −10°, several drops of concentrated sulfuric acid were added, and then at the same temperature, over a period of 15 minutes, a solution of 15 g (0.18 mole) diketene in 10 ml ether was added dropwise. The mixture was heated for 1 hour (the end of the reaction was determined by the disappearance of the odor of diketene). The ether was removed, and the remaining mass quickly crystallized. After separating the crystals on a porous plate, the product obtained had m.p. of 49°; the yield was 17.9 g (63.9%).

2. Benzeneazoacetoacetylphenol (II). 1.78 g acetoacetylphenol was dissolved, with vigorous stirring, in 100 ml ethyl alcohol and 10 ml 0.1 N solution of sodium acetate. The solution was cooled, and to it, over a period of 2 hours, with cooling and stirring, 110 ml 0.1 N solution of diazobenzene was added. On addition of the diazo-solution, a dye precipitated — small yellow needles (from alcohol), m.p. 95-96°; the yield was 1.78 g (64%).

0.1502 g sub.: 13.5 ml N_2 (19°, 744 mm). 0.1760 g sub.: 14.4 ml N_2 (18°, 744 mm). Found %: N 10.07, 9.83. $C_{18}H_{14}O_3N_2$. Calculated %: N 9.93.

A solution of 0.28 g of the azo dye (II) in 10 ml of a 5% solution of hydrochloric acid was boiled for 1 hour. On cooling the solution, yellow crystals, m.p. of 155° (from alcohol) were precipitated. The sample, mixed with specially synthesized α-benzeneazoacetoacetic acid (m.p. 159-160°) melted at 155°; the yield was 0.17 g (86%).

3. 4-Methylcoumarin (III). 1.5 g acetoacetylphenol was dissolved in 15 ml of concentrated sulfuric acid (d 1.84); after 20 hours the solution was poured onto ice and treated with ether; the ether extract was washed with a 5% solution of sodium hydroxide; after the ether was removed, crystals of 4-methylcoumarin [11], m.p. of 80° (from benzene) remained; the yield amounted to a few percent.

4. Acetoacetylguaiacol (IV). 6.2 g (0.05 mole) guaiacol was dissolved in 50 ml benzene. To the solution, cooled to −10°, several drops of pyridine were added, and over a period of 10 minutes 4.5 g (0.053 mole) diketene was added. The solution was heated for 1.5 hours; the benzene was removed; the viscous liquid remaining quickly crystallized. The acetoacetylguaiacol consisted of colorless plates, m.p. 62-63° (from alcohol), yield of 7.07 g (68% of the theoretical, based on guaiacol).

0.1305 g sub.: 0.3023 g CO_2; 0.0728 g H_2O. 0.1165 g sub.: 0.2698 g CO_2; 0.0639 g H_2O. 0.1807 g sub.: 16.35 g C_6H_6: Δt 0.31°. 0.1773 g sub.: 4.503 g C_6H_6O: Δt 0.35°. Found %: C 63.22, 63.22; H 6.24, 6.14. M 181.9, 187.8. $C_{11}H_{12}O_4$. Calculated %: C 63.45; H 5.81. M 208.2.

When the reaction was carried out with traces of concentrated sulfuric acid in the ether, the yield of (IV) was 58.6%.

5. Benzeneazoacetoacetylguaiacol. 2.08 g (0.01 mole) acetoacetylguaiacol was dissolved in a mixture of 110 ml ethyl alcohol and 10 ml 0.1 N solution of sodium acetate. To the solution cooled to 0°, over a period of 1.5 hours, 110 ml (0.011 mole) 0.1 N solution of diazobenzene was added with stirring. On addition of the diazo-solution, a yellow azo dye, m.p. 95-97° (from alcohol) gradually precipitated; the yield was 2.5 g (83%).

0.1541 g sub.: 12.1 ml N_2 (18°, 751 mm). 0.1598 g sub.: 12.3 ml N_2 (17°, 760 mm). Found %: N 8.89, 8.90. $C_{17}H_{16}O_4N_2$. Calculated %: N 8.97.

6. Monoacetoacetylhydroquinone (VI). 3.3 g (0.03 mole) hydroquinone was mixed with 30 ml benzene. To the mixture cooled to −10°, over a period of 10 minutes, several drops of pyridine and later 2.8 g (0.033 mole) diketene were added. After boiling the mixture for 2 hours and removing the benzene, a viscous, cinnamon-yellow liquid remained, which quickly crystallized. By treatment of the crystalline mass with 30 ml hot chloroform the reaction product was separated from the unreacted hydroquinone, which did not dissolve in hot chloroform. From the cooled chloroform filtrate monoacetoacetylhydroquinone precipitated as white needles, m.p. 102° (from chloroform), and readily soluble in acetone, ether, and methyl alcohol, less soluble in ethyl alcohol and benzene; it was insoluble in chlorobenzene and petroleum ether; the yield was 5.3 g (91%).

0.1113 g sub.: 0.2532 g CO_2; 0.0543 g H_2O. 0.1130 g sub.: 0.2572 g CO_2; 0.0549 g H_2O. 0.1076 g sub.: 7.286 g C_6H_6O: Δt 0.14°. 0.1300 g sub.: 5.28 g C_6H_6O: Δt 22°. Found %: C 62.09, 62.10; H 5.46, 5.43. M 176.2, 186.9. $C_{10}H_{10}O_4$. Calculated %: C 61.84; H 5.19. M 194.18.

In order to carry out the hydrolysis, a solution of 0.97 g (0.005 mole) monoacetoacetylhydroquinone in 25 ml of a 5% aqueous solution of sodium hydroxide was heated on a boiling water bath. On acidification of the solution, hydroquinone was precipitated quantitatively; acetone was detected by the reaction with o-nitrobenzaldehyde (formation of indigo).

7. Diacetoacetylhydroquinone (VII). a) 0.3 g (0.03 mole) hydroquinone was mixed with 30 ml benzene. To the mixture at −10° several drops of pyridine were added, and then, over a period of 15 minutes, 5.6 g (0.066 mole) diketene was added dropwise; the mixture was boiled for 2 hours. After concentrating and cooling the benzene solution, diacetoacetylhydroquinone precipitated as white crystals, m.p. 121-122° (from ethyl alcohol); the crystals were soluble in acetone and chloroform, less soluble in ethyl alcohol; they did not dissolve in water, ether, methyl alcohol, or benzene; the yield was 7.4 g (88.7%).

0.1226 g sub.: 0.2731 g CO_2; 0.0532 g H_2O. 0.1024 g sub.: 0.2258 g CO_2; 0.0501 g H_2O. Found %: C 60.80, 60.17; H 4.85, 5.47. $C_{14}H_{14}O_6$. Calculated %: C 60.53; H 5.07.

b) To a solution of 1.94 g (0.01 mole) monoacetoacetylhydroquinone in 40 ml of benzene at −10°, several drops of pyridine and 1.2 g (0.014 mole) diketene were added; the solution was boiled for 1.5 hours. The crystalline mass remaining after removal of the benzene was freed of a gum formation, and was then drawn off onto a porous plate; the product melted at 122° (from ethyl alcohol). The sample, when mixed with the known substance described above, caused no m.p. depression; the yield was 2.34 g (84%).

8. Disbenzeneazodiacetoacetylhydroquinone (VIII). 1.39 g (0.005 mole) diacetoacetylhydroquinone was suspended in 150 ml of ethyl alcohol mixed with 40 ml of 0.1 N solution of sodium acetate. To the suspension, cooled to −1°, over a period of 1.5 hours, 100 ml (0.01 mole) 0.1 N solution of diazobenzene was added, with vigorous stirring; gradually, a dye consisting of orange needles, m.p. 226-227° (from acetic anhydride), was precipitated; it was insoluble in alcohol, benzene and toluene; the yield was 2.36 g (97%).

0.1067 g sub.: 10.8 ml N_2 (17°, 760 mm). 0.0963 g sub.: 9.6 ml N_2 (17°, 760 mm). Found %: N 11.70, 11.53. $C_{26}H_{22}O_6N_4$. Calculated %: N 11.52.

9. Acetoacetyl-p-cresol (IX). 2.16 g (0.02 mole) p-cresol was dissolved in 35 ml of benzene, the solution was cooled to −10°, and to it several drops of pyridine and 2 g (0.024 mole) diketene were added successively. The solution was boiled for 1 hour, and the benzene was removed; a viscous, oily liquid remained, which crystallized on cooling. The acetoacetyl-p-cresol consisted of long needles, m.p. 68° (from alcohol); the yield was 3.55 g (92.5%).

0.0735 g sub.: 0.1857 g CO_2; 0.0433 g H_2O. 0.0638 g sub.: 5.026 g C_3H_6O; Δt 0.11°. Found %: C 68.95; H 6.66. M 193.3. $C_{11}H_{12}O_3$. Calculated %: C 68.93; H 6.29. M 192.2.

10. Acetoacetyl-p-bromophenol (X). To a solution of 4.3 g (0.025 mole) p-bromophenol in 40 ml of benzene, cooled to −10°, several drops of pyridine were added, and 2.2 g (0.026 mole) diketene was added dropwise. The solution was boiled for 1 hour after the benzene was removed, crystals of acetoacetyl-p-bromophenol having a m.p. of 54°, remained; the yield was 4.7 g (74.5%).

11. 3-Acetylcoumarin (XI). To a mixture of 1.2 g (0.01 mole) salicylaldehyde and 0.1 g anhydrous potassium acetate at 35-40°, over a period of 1.5 hours, 0.84 g (0.01 mole) diketene was added. The mass was poured into 25 ml of 5% hydrochloric acid solution; from the oily layer benzene was removed. The 3-acetylcoumarin [12] consisted of colorless crystals, m.p. 120-121° (from ligroin and from 50% aqueous alcohol); the yield was 83.7%; in the presence of pyridine the yield was 40.4%.

SUMMARY

1. A method was developed for obtaining acetoacetyl derivatives of some aromatic hydroxy compounds.

2. It was shown that the synthesis of acetoacetyl derivatives is accomplished by using basic catalysts (pyridine), and in some cases acidic catalysts (sulfuric acid).

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ALKYLATION OF DIPHENYL BY ALCOHOLS IN THE PRESENCE OF PHOSPHORIC ACID

I. A. Romadan and V. K. Berzinya

Judging from the data in the literature, the alkyl diphenyls have been comparatively little investigated, and methods for obtaining them by direct alkylation are few. Thus, Pokrovskaya and Sushchik [1] alkylated diphenyl with hexyl bromide, using aluminum chloride, and obtained a mixture of mono-, di- and trihexyldiphenyl (an oil having a solidification point of −36°) in a total yield of 80%. On alkylation of diphenyl with propylene and isopropyl chloride in the presence of $AlCl_3$, mono- and diisopropyldiphenyl were obtained as a viscous oil having a solidification point of −40° [2].

The purpose of our work was the alkylation of diphenyl by butyl and amyl alcohols in the presence of phosphoric acid (d 1.86-1.87), which is a mild condensing agent, which permits the production of, chiefly, the monosubstituted compound, and directs the radical into the para-position.

We effected the alkylation of diphenyl with normal, iso- and tertiary-butyl alcohols, and also with iso- and tertiary-amyl alcohols. The condensations were carried out in an apparatus fitted with a mechanical stirrer and a reflux condenser. The alcohols were used in excess with respect to diphenyl, since they also served as solvents (3-3.5 moles of alcohol to 1 mole of diphenyl and up to 4 moles of phosphoric acid).

The reaction mixture was heated for 10-20 hours at the determined optimal temperature. The yields of the alkyl diphenyls depended to a great extent on the temperature: on alkylation with amyl alcohol the best yields were obtained at 120-125°; at 100-110° almost all of the diphenyl was recovered, unreacted, and the reaction mass represented amyl phosphate, the yield of the amyldiphenyl not exceeding 20-25%. At 140-150° the diphenyl also was unaltered, the reaction mixture separated into two layers, and the upper layer consisted of a mixture of unsaturated hydrocarbons boiling at 150-205° – the dimer and trimer of isoamylene, with the former predominating.

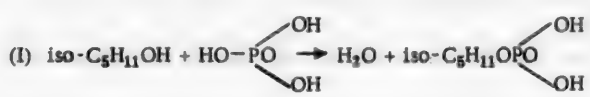
The alkylation of diphenyl by butyl alcohol proceeded at 90-110°, depending on the structure of the alcohol. At the higher temperatures chiefly the dimer and trimer of isobutylene were obtained.

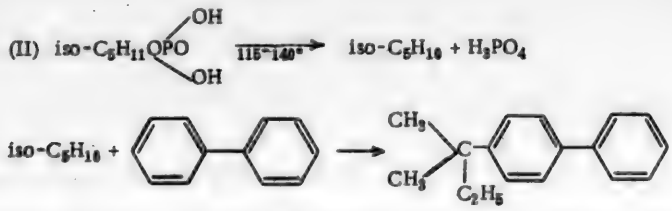
The problem of the mechanism of the alkylation of aromatic compounds in the presence of phosphoric acid had not been worked out completely until now. It was assumed that the alkylating agent was the ester [3].

On the basis of a series of experiments, we came to the conclusion that the alkylation of diphenyl does not proceed by way of the phosphates, but by way of hydrocarbons, which are formed by the splitting off of the phosphoric acid from the ester, to form an intermediate product. The resulting phosphates were stable in the range of 90-115° (depending on the nature of the alcohol). In the 120-125° range, comparatively slow decomposition of the esters with formation of unsaturated hydrocarbons occurs, and these hydrocarbons also react with diphenyl. At higher temperatures, the rate of decomposition of the esters increases, but at the same time, the rate of polymerization of butylene and amylene increases, exceeding the rate of alkylation.

To elucidate the mechanism of alkylation of diphenyl by alcohols in the presence of phosphoric acid, we investigated the reaction between isoamyl alcohol and phosphoric acid, at different temperatures. By heating the mixture at 90-95°, the phosphate was obtained, and it was then converted to the barium salt. At the indicated temperatures and even in the 110-115° range, we observed no separation of the reaction mass into two layers, which indicated the absence of unsaturated hydrocarbons; at a higher temperature we observed the separation of the reaction mass, the upper layer consisting of a mixture of the dimer and trimer of isoamylene. The rate of formation of the polymers increased with the temperature. In the presence of comparatively large quantities of unsaturated hydrocarbons, we could not observe even traces of the phosphate.

Hence, we came to the conclusion that the alkylation of diphenyl by alcohols proceeds according to the following scheme:





On alkylation with isoamyl and isobutyl alcohols, alkyl diphenyls having tertiary radicals were obtained, which indicates isomerization of the radicals during the reaction process.

On alkylation with tertiary alcohols, the reactions were practically complete after 5-6 hours; for alcohols having an iso-radical the time of heating amounted 10-12 hours. The normal alcohols reacted more difficultly and required heating from 15 to 20 hours.

In this way we obtained chiefly, as expected, mono-alkyl diphenyls having the radical in the p-position. The yields of the dialkyl diphenyls were small (2-6%).

On alkylation of diphenyl with n-butyl alcohol, an oily product was obtained, with b.p. 292-296°, M 209 (calculated for mono-butyldiphenyl, M 210), and a solidification point of −43°. The structure of the radical was not elucidated, therefore we cannot say whether isomerization occurs. This substance had not been described in the literature.

On alkylation with iso- and with tert-butyl alcohols, we obtained identical crystalline substances, with m.p. of 52° and a b.p. of 282-285°. This substance corresponded to the p-tert-butyldiphenyl obtained by Schreiner [4].

A similar isomerization was observed on alkylating diphenyl with sec- and tert-amyl alcohols; in both cases, we obtained the same oily substance, not described in the literature, but having a b.p. of 304-305°, M, 221 (by calculation, 224), and a solidification point of −26°.

TABLE 1

Products of the Alkylation of Diphenyl by Alcohols

Substance	Temperature			d_4^{20}	n_D^{20}	M		Viscosity (in poises)		Viscosity index
	boiling	melting	solidification			found	calc'd	20°	30°	
p-Tert-amyldiphenyl (from isoamyl alcohol)*	300-305°	–	−26	0.9964	1.5630	212	224	20.08	5.28	3.83
p-Tert-amyldiphenyl (from tert-amyl alcohol)	300-305	–	−23	0.9955	1.5628	217	224	19.94	5.26	3.78
Diamyldiphenyl	312-316	–	–	0.9993	1.5709	281	294	Not determined		
p-Tert-butyldiphenyl (from isobutyl alcohol)	280-285	52	–	–	–	–	–	–	–	–
p-Tert-butyldiphenyl (from tert-butyl alcohol)	280-285	52	–	–	–	205	210	–	–	–
Monobutyldiphenyl (from n-butyl alcohol)**	292-296	–	−43	0.9973	1.5710	207	210	22.14	6.17	3.75
Dibutyldiphenyl (from n-butyl alcohol)	305-307	–	−30	0.9977	1.5700	252	266	Not determined		

The position of the radical was established by oxidation of the substance by heating with 5% nitric acid in a sealed tube at 170° for 10 hours.*** In all cases, only terephthalic acid was obtained.

* 2786 mg sub.: 9.3008 mg CO_2; 1.685 mg H_2O. Found %: C 91.16; H 8.71. $C_{17}H_{20}$. Calculated %: C 91. H 8.98.

** 4.086 mg sub.: 13.7000 mg CO_2; 3.314 mg H_2O. Found %: C 91.48; H 9.03. $C_{16}H_{18}$. Calculated %: C 91.33; H 8.57.

*** On oxidation with chromic anhydride and potassium permanganate the oily layer did not disappear upon heating for 50 hours.

The viscosity of the oily product obtained was measured in an Ostwald viscosimeter. The viscosity values, in poises, are presented in Table 1.

If the viscosity values for the alkyl naphthalenes are compared [5, 6] with the viscosities of the alkyl diphenyls, the latter are small in absolute value, whereas the alkyl diphenyls have the more sloping viscosity curves as is obvious from the $\eta_{20}:\eta_{50}$ ratio given in Table 1.

The temperatures of solidification of the oily substances were comparatively low, as shown in the same Table.

TABLE 2

Conditions of Alkylation of Diphenyl by Alcohols and Yields of the Crude Products

Alcohol	Quantity (in g)			Duration of heating (hrs)	Temperature of heating	Yield of crude product		Boiling point of crude product
	diphenyl	alcohol	catalyst			(g)	(%)	
Isoamyl	10	25	65	20	120-125°	8.5	58	290-310°
	10	25	65	20	125-130	8.3	57	290-310
	10	25	65	20	130-135	7.4	51	290-310
	10	25	65	20	145-150	6	41	290-310
	10	25	80	20	120-130	8.7	60	290-310
Tert-amyl	5	20	80	10	100-105	3	41.5	290-310
	10	20	80	10	110-115	4.4	58	290-310
Isobutyl	10	40	65	20	115-120	1.8	13	270-290
	10	40	65	20	95-100	5.5	40.4	270-290
	10	40	65	10	95-100	2.7	20	270-290
	10	20	100	20	95-100	6.4	46	270-290
	10	20	100	10	95-100	6	44	270-290
Tert-butyl	5	14	80	10	85-90	3.2	46	280-285
n-Butyl	10	40	80	20	100-105	4.9	36	287-296

EXPERIMENTAL

Alkylation of Diphenyl by Alcohols

After completion of the reaction carried out under the conditions described above, the reaction mixture was poured into an equal quantity of water, and the upper layer was separated. The unaltered diphenyl was steam-distilled, but the alkyl diphenyl remained in the flask as an oily substance. The oil was separated, dried over calcium chloride, and distilled twice over metallic sodium. The experimental data are recorded in Tables 1 and 2. On determination of the molecular weight, the value obtained was smaller than that obtained by calculation, since diphenyl was not completely removed.

Preparation of Isoamyl Phosphate

1. 40 g of isoamyl alcohol and 65 g of phosphoric acid were heated at 90-95° for 10 hours. At these temperatures the mass did not sepatate into two layers. The reaction mass was poured into a small quantity of water (10-12 ml), and the unreacted isoamylalcohol was removed in a separatory funnel. To the remaining acid solution was added 500 ml of water, and then small portions of barium hydroxide were introduced until the solution was slightly alkaline (to litmus). The barium phosphate which precipitated was filtered off. Carbon dioxide was passed into the mother liquor, and the precipitated barium carbonate was filtered off. From the mother liquor concentrated on the water bath, crystals of the barium salt of isoamyl phosphate precipitated. After recrystallization from alcohol, well-defined, colorless crystals were obtained.

Found %: Ba 45.28; P 10.24. $C_5H_{11}O_4PBa$. Calculated %: Ba 45.00; P 10.20.

2. On heating the same quantities of reagents for 10 hours at 120-125°, a separation of the mass into two layers was observed. The upper layer consisted of a mixture of the dimer and trimer of isoamylene; 8 g was obtained. The lower layer contained isoamyl phosphate.

3. The proportion of the reagents was the same. They were heated for 10 hours at 130-135°. 14 g of unsaturated hydrocarbons were obtained, but the phosphate was not observed. The unsaturated compounds obtained

were washed, dried and fractionally distilled. The 3 fractions, having b.p.'s of 155-160, 195-200 and 200-205° were separated. Results of the determinations of molecular weights and iodine numbers are given in Table 3.

TABLE 3

Boiling point	Molecular weight		General formula	Iodine number	
	found	calculated		found	calculated
155-160°	145	140	$C_{10}H_{20}$	178	181
195-200	165	Mixture		140	Mixture
200-205	198	210	$C_{15}H_{30}$	106	120

Judging from the data given, the fraction with b.p. 155-160° corresponded to the dimer of isoamylene having the formula $C_{10}H_{20}$; the fraction with b.p. 200-205° corresponded approximately to the trimer of isoamylene, for which the calculated iodine number was equal to 120, and the molecular weight was equal to 210; the middle fraction (b.p. 195-200°) was a mixture of the dimer and trimer.

SUMMARY

1. A method for the alkylation of diphenyl by alcohols in the presence of phosphoric acid was developed, and the mechanism of the reaction was elucidated.

2. It was found that in the presence of phosphoric acid, chiefly the monoalkyl diphenyls were formed, and in them the secondary radical isomerized to the tertiary structure and was located in the p-position.

3. p-Tert-amyldiphenyl and p-butyldiphenyl, which were unknown in the literature, were obtained.

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CYANOETHYLATION OF THE NUCLEUS OF AROMATIC COMPOUNDS

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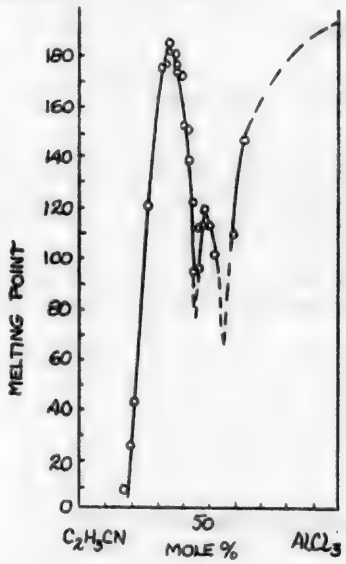
We found earlier [1] that allylnitrile readily adds to benzene in the presence of $AlCl_3$, forming the nitrile of β-phenylbutyric acid in almost quantitative yield. At the same time, acrylonitrile is characterized by its great passivity in the Friedel-Crafts reaction. This reaction with benzene had not been successful until the present time [1, 2]; only the cyanoethylation of the nucleus of phenol [2] and polyatomic phenols [3] was known. We set ourselves the problem of finding the source of the low reactivity of acrylonitrile in these syntheses, and of determining conditions under which it was feasible to carry out the cyanoethylation of the nucleus of various aromatic compounds.

It is well-known that the great activity of the double bond of acrylonitrile [3] is determined by the polarization force of its molecule. The direction of the polarization $CH_2=\overrightarrow{CH}-C\equiv\overleftarrow{N}$ is determined by the clearly expressed electrophilic character of acrylonitrile, which should promote the alkylation of the aromatic nucleus.



Fusibility diagram of the system acrylonitrile—aluminum chloride.

We assumed that the passivity of acrylonitrile in the presence of $AlCl_3$ was connected with the changes, which were introduced by complex formation at the nitrile group, in the mutual effect of this group and the double bond. Apparently, the individual stability of the complex forming is of decisive value. It is known that some unsaturated ketones [4] and nitro-compounds [5, 6], in molecules in which an electronegative group binding $AlCl_3$ in the complex is joined to a double bond, react with benzene without difficulty.

On the basis of literature data on the heats of complex formation of benzonitrile [7], acetophenone and nitrobenzene [8], it is possible to estimate the relative stabilities of the complexes of the corresponding α,β-unsaturated compounds with $AlCl_3$. The nitrile complex should be the most stable in this series.

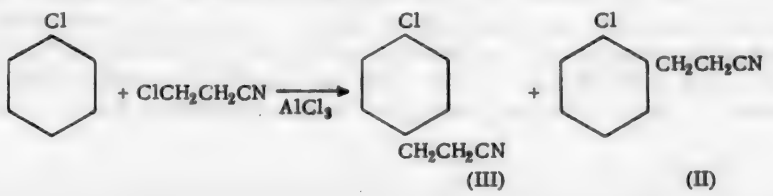
A thermal analysis of the system $AlCl_3 \cdot C_2H_3CN$ (figure) confirmed the assumption concerning the high stability of this complex. The fusibility curve had two sharply expressed maxima — one at 118°, corresponding to the compound $Al_2Cl_6 \cdot 2C_2H_3CN$, and the other at 181°, corresponding to the compound $Al_2Cl_6 \cdot 4C_2H_3CN$.

We also studied the influence of HCl on the cyanoethylation of benzene. It was shown that, on saturation of a benzene solution of acrylonitrile with hydrogen chloride, followed by introduction of 1.5-3.5 moles of $AlCl_3$, the nitrile of hydrocinnamic acid was obtained in good yield (55-66%). Condensation of the β-propionitrile proceeded in the same manner.

$$CH_2=CH-CN \xrightarrow{+HCl} ClCH_2CH_2CN \xrightarrow[AlCl_3]{+C_6H_6} \underset{(I)}{C_6H_5CH_2CH_2CN}.$$

HCl did not promote the reaction, if the reaction mixture was saturated after the addition of $AlCl_3$. Hence, we came to the conclusion that complex formation impedes the addition of HCl to the double bond of acrylonitrile. This was directly confirmed experimentally: on saturation of a benzene solution of acrylonitrile, in the presence of $AlCl_3$, by HCl, not even traces of β-chloropropionitrile were obtained. The method developed for the synthesis of the nitrile of hydrocinnamic acid is considerably simpler than that described earlier, and is of preparative interest.

By the condensation of β-chloropropionitrile with chlorobenzene, a mixture of the nitriles of o- and p-chlorohydrocinnamic acids was obtained in a total yield of 65%:



Next, the condensation of acrylonitrile with o-xylene and mesitylene was studied, the hydrogens of the nuclei of these compounds being more mobile than in benzene [9, 10]. These hydrocarbons were cyanoethylated directly by acrylonitrile by using 2-3.5 moles of $AlCl_3$. A mixture of nitriles, in a yield of about 50%, was obtained. From the reaction products from o-xylene, the nitrile of p-methylhydrocinnamic acid (IV) was obtained.

On the basis of these experiments, we came to the conclusion that the capacity of the double bond of acrylonitrile for addition reactions in its $AlCl_3$ complex was weakened, but not destroyed. It might be expected that a considerable increase of the temperature, diminishing the stability of the complex, would favor the cyanoethylation reaction. On carrying out reactions of acrylonitrile with benzene (in an autoclave) and chlorobenzene at 140-180° with 2.5-3.5 moles of $AlCl_3$, the corresponding aliphatic-aromatic nitriles were obtained, but in small yields (12-27%).

In order to elucidate the relationship of the reactivity of the double bond, joined to the nitrile group, to the stability of the intermediate complex with $AlCl_3$, we studied the condensation of benzene with the nitriles of γ,γ,γ-trichlorocrotonic acid (V) and cinnamic acid.

Accumulation of chlorine atoms at the α-position to the carboxyl group diminished the stability of the complex of BF_3 with the acids [11]. The complexes of the halogenonitriles with $AlCl_3$ were more easily broken down to their components on heating, than were the compounds with acetonitrile [12, 13]. The phenyl group shows the same effect: the stabilities of the complexes with $AlCl_3$ diminish in the series: $C_6H_5CHO \cdot AlCl_3 > C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}O \cdot AlCl_3 >$ $> C_6H_5\underset{\displaystyle C_6H_5}{\underset{|}{C}}O \cdot AlCl_3$ [8]. The basicity of the nitrile group also decreases on going from the acetonitrile to phenylacetonitrile [14]. Since the double bond did not create an obstacle to the transfer of the effects of the halide and phenyl groups, we expected that the stability of the nitrile complexes of γ,γ,γ-trichlorocrotonic (V) and cinnamic acids would be considerably weakened, and that condensation with them would proceed easily.

Our expectations were confirmed. The nitrile of γ,γ,γ-trichlorocrotonic acid (V) with 1.2 moles of $AlCl_3$ on heating with benzene for 5 hours at 60-70°, yielded the nitrile of β-phenyl-γ,γ-dichlorovinylacetic acid (VI) in a yield of 63% of the theoretical:

$$C_6H_6 + Cl_3CCH{=}CH{-}CN \xrightarrow{AlCl_3} \left[Cl_2C{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}H{-}CH_2CN \right] \xrightarrow{-HCl} Cl_2C{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}CH_2CN$$

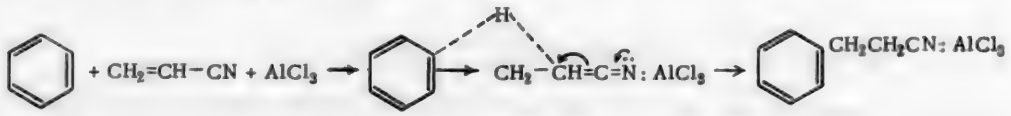
(V) (VI)

The nitrile of cinnamic acid was condensed with benzene in the presence of 1.5 moles of $AlCl_3$ at 80°, and gave the nitrile of β,β-diphenylpropionic acid in a yield of 93%:

$$C_6H_6 + C_6H_5CH{=}CH{-}CN \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_2CN$$

(VII)

We assume that the present reaction, like all Friedel-Crafts syntheses, proceeds through the triple complex of reactants with $AlCl_3$, according to the scheme:



The 1,4-addition of benzene to acrylonitrile by this mechanism, when the formation of new and the rupture of old bonds proceeds simultaneously in the triple complex, is not very probable because of the excessive distance to the hydrogen-acceptor - nitrogen atom, and also because of the diminishing basic properties of nitrogen after formation of the complex; therefore, we assumed that the reaction proceeded as the 1,2-addition. The passivity of the double bond of acrylonitrile could then be accounted for by the fact that the additional polarization of the molecule, under the influence of the complex connected to $AlCl_3$, decreases the mobility of the electrons in the system of conjugated bonds, and makes it more difficult for the reaction to proceed according to the scheme presented. The decrease of the stability of the complex under the influence of the electronegative group or on increase of the temperature, increases the mobility of the electrons and, consequently, facilitates the reaction.

EXPERIMENTAL

Thermal Analysis of the System Acrylonitrile–Aluminum Chloride

We used acrylonitrile, carefully purified and having the following constants: b.p. 75.4-75.5° (718 mm), d_4^{20} 0.8063, n_D^{20} 1.3911. $AlCl_3$ of "purified" grade was mixed with freshly cut Al and sublimed. The completely white $AlCl_3$, containing no iron, was sealed in a small ampoule.

The measurements were made in a small cryoscope fitted with a side tube having a ground-glass stopper. In the cryoscope, through rubber stoppers were inserted a thermometer, a platinum stirrer, and a small tube containing H_2SO_4, to keep moisture from the air from getting in.

To a definite weight of $AlCl_3$, the nitrile was quickly added from a dropper through the tube; its quantity was determined by differences in the weight of the dropper. A cooling curve was obtained for each mixture. The temperature was recorded every 30 seconds. A discontinuity on the cooling curve corresponded to the temperature of the appearance of the first crystals. Each determination was repeated 3-4 times, until replicate results were obtained. The fusibility curves obtained are shown in the Figure. For 0 to 17 mole % of $AlCl_3$ we did not succeed in determining the temperature of crystallization because of strong supercooling, and at 66 to 100 mole %—because of the volatilization of $AlCl_3$.

Condensation of β-Chloropropionitrile with Benzene and Chlorobenzene

The condensation was carried out in a three-necked flask, fitted with a stirrer, thermometer and reflux condenser, which through a calcium chloride tube was connected to a Tishchenko bottle for absorbing the HCl. To a solution of β-chloropropionitrile and the aromatic compound, portions of $AlCl_3$ were added. Dissolution was accompanied by the evolution of heat and by the appearance of a bright color: green for the reaction with benzene, and red for the reaction with chlorobenzene. Moreover, a voluminous white precipitate of the complex deposited. The mixture was heated on a water bath or grid until the evolution of HCl abated. The excess $AlCl_3$ and the complex were gradually dissolved. The reaction mixture was decomposed by dilute hydrochloric acid. The reaction products were extracted with benzene or ether, washed with water, and dried over $CaCl_2$. After removal of the solvent, the residuals were fractionally distilled in vacuo.

By a series of experiments we determined the effects of the quantity of $AlCl_3$, the reaction temperature and the duration of reaction.

β-Chloropropionitrile–benzene. 10 g of β-chloropropionitrile, 26 g of benzene, and 51.3 g of $AlCl_3$ were used. The molar ratio was 1:3:3.5. The mixture was heated for 29 hours at 80-98°. 10 g (69%) of the nitrile of hydrocinnamic acid (I) was obtained:

B.p. 125-126° at 15 mm, n_D^{20} 1.5266, d_4^{20} 1.0016, MR_D 40.18; calculated 39.99.

The amide of hydrocinnamic acid. To a solution of 2.7 g (0.026 mole) of nitrile (I) in 10 ml of alcohol was added 10.5 ml of 20% H_2O_2, and then 0.9 ml of a 6 N solution of NaOH. After heating slightly, an exothermic reaction began with the liberation of oxygen. The temperature for cooling was maintained at 45-50°. For completion of the reaction, the mixture was heated at the same temperature for 1 hour on the water bath. After neutralization with 5% H_2SO_4, the alcohol was removed until the mixture separated into two layers. On cooling, the lower layer crystallized. 2.6 g of the amide of hydrocinnamic acid was obtained. After recrystallization from benzene its m.p. was 99-100°. The sample, mixed with the amide obtained from hydrocinnamic acid, caused no m.p. depression.

β-Chloropropionitrile–chlorobenzene. 10 g of β-chloropropionitrile, 25 g of chlorobenzene, and 43.8 g of $AlCl_3$ were used. The molar ratio was 1:2:3. The mixture was heated for 25 hours at 140°. 11.9 g (64.6%) of a mixture of the nitriles of o-chlorohydrocinnamic (II) and p-chlorohydrocinnamic (III) acids was obtained. The crude product had b.p. 140-159° at 15 mm and was fractionally distilled in vacuo. The following three fractions were obtained: 1st, 140-145° at 15 mm; 2nd, 148-153° at 15 mm; and 3rd, 153-156° at 15 mm.

The nitrile of o-chlorohydrocinnamic acid (II):

B.p. 140-145° at 15 mm; n_D^{20} 1.5390, d_4^{20} 1.1390; MR_D 45.51; calculated 44.85.

o-Chlorohydrocinnamic acid. 2.5 g of nitrile (II) was boiled at 145-150° with 50% H_2SO_4 for 1.5 hours. After cooling, the upper layer crystallized. The acid obtained was purified by reprecipitation from a soda solution, and was recrystallized from petroleum ether. 3.3 g of o-chlorohydrocinnamic acid having a m.p. of 95.5-96.5° was obtained. The literature [15] gives m.p. 96.5-97° for this acid.

The nitrile of p-chlorohydrocinnamic acid (III):

B.p. 153-156° at 15 mm, n_D^{20} 1.5400, d_4^{20} 1.1532, MR_D 45.03; Calculated 44.85.

The amide of p-chlorohydrocinnamic acid, obtained in the same way as the amide from hydrocinnamic acid, had a m.p. of 129-130° (from benzene).

4.49 mg sub.: 0.315 ml N_2 (16°, 742 mm). Found %: N 8.10. $C_9H_{10}NOCl$. Calculated %: N 7.63.

p-Chlorohydrocinnamic acid, obtained in the same way as the o-isomer, had a m.p. of 121-122.5°. According to the literature [15] the m.p. is 122-123° (from petroleum ether).

Condensation of acrylonitrile with benzene with preliminary saturation of the reaction mixture with HCl. A solution of 6.8 g (0.13 mole) acrylonitrile in 29.9 g (0.38 mole) benzene, cooled with ice, was saturated for 3 hours with HCl, and then kept at room temperature for 12-15 hours. After addition of 60 g (0.45 mole) of $AlCl_3$, the mixture was heated for 30 hours at 84-98°. The reaction products were separated as usual. 11 g (66%) of the nitrile of hydrocinnamic acid (I) was obtained:

B.p. 125-126° at 15 mm, n_D^{20} 1.5266, d_4^{20} 1.0016, MR_D 40.18; claculated 39.99.

The amide obtained had a m.p. of 100°, and produced no melting point depression with the known amide of hydrocinnamic acid.

Condensation of acrylonitrile with mesitylene, o-xylene and chlorobenzene. A portion of $AlCl_3$ was added to a solution of acrylonitrile in an aromatic compound. In order to dissolve all of the $AlCl_3$ and the precipitated complex, the mixture was heated on the water bath. Then the heating was carried out on the grid. The evolution of HCl, observed at first, quickly ceased. The reaction mixture was treated in the same way as for the reaction with β-chloropropionitrile.

Acrylonitrile–mesitylene. 6.8 g acrylonitrile, 22.8 g mesitylene, and 52.5 g of $AlCl_3$ were used. The molar ratio was 1:1.5:3. The mixture was heated for 9.5 hours at 130-135°. 8.9 g of a fraction at 128-138° at 12 mm (47%, based on the nitrile of methylhydrocinnamic acid) was obtained.

For determination of the physical constants and for analysis, the 129-133° fraction at 12 mm, n_D^{20} 1.4822, d_4^{20} 0.9437, MR_D 43.8, was taken; calculated for the nitrile of methyl hydrocinnamic acid, 44.6.

3.86 mg sub.: 0.322 ml N_2 (23°, 719.5 mm).. Found %: N 9.12. $C_{10}H_{11}N$. Calculated %: N 9.65.

Saponification with 50% H_2SO_4 gave an acid in the form of a viscous oil having a b.p. of 150-159° at 5 mm, which failed to crystallize.

On reduction with sodium in anhydrous alcohol, we obtained an amide with b.p. 116-122° at 12 mm. We obtained the amide picrate having a m.p. of 143-153°, from which 7 recrystallizations from alcohol yielded a fraction having a m.p. of 164-167°.

Acrylonitrile–o-xylene. 6.4 g acrylonitrile, 41.3 g o-xylene and 48.2 g $AlCl_3$ were used. The molar ratio was 1:3:3. The mixture was heated for 9 hours at 130°. 9.7 g (55.4%, based on the nitrile of methylhydrocinnamic acid) of a crude product, b.p. 124-160° at 15 mm, was obtained. After distillation in vacuo, the following fractions were obtained: 1st, 124-131°; 2nd, 131-136°; 3rd, 137-141°; and 4th, 147-154° at 15 mm.

Nitrile of methylhydrocinnamic acid (the structure was not elucidated):

B.p. 131-136° at 15 mm, n_D^{20} 1.4947, d_4^{20} 0.9589, MR_D 44.07; calculated 44.6.

Saponification with 50% H_2SO_4 produced an acid having a b.p. of 125-127° at 3 mm.

0.2219 g sub.: 11.90 ml 0.0927 N KOH. Found: M 172.9. $C_{10}H_{12}O_2$. Calculated: M 164.

The nitrile of p-methylhydrocinnamic acid (IV):

B.p. 137-141° at 15 mm [15], n_D^{20} 1.4988, d_4^{20} 0.9628, MR_D 44.2; calculated 44.07.

Found %: N 9.27. $C_{10}H_{11}N$. Calculated %: N 9.65.

p-Methylhydrocinnamic acid was obtained by boiling the nitrile with 50% H_2SO_4. The melting point after recrystallization from petroleum ether was 116-117°. According to data in the literature, the m.p. is 116 and 120° [15].

Found: M 166.7. $C_{10}H_{12}O_2$. Calculated: M 164.0.

Oxidation of p-methylhydrocinnamic acid by an alkaline solution of $KMnO_4$ gave terephthalic acid which was converted by diazomethane to the dimethyl ester having a m.p. of 138-140° (from alcohol). The sample when mixed with the known ester of terephthalic acid produced no m.p. depression.

Mixture of nitriles of dimethylhydrocinnamic acids:

B.p. 147-154° at 15 mm, n_D^{20} 1.5160, d_4^{20} 0.9758, MR_D 49.21; calculated 49.33.

Saponification by 50% H_2SO_4 yielded an acid with b.p. of 130-140° at 3 mm. On prolonged standing, the acid partially crystallized. The melting point of the crystals (from petroleum ether) was 105-107°. The melting points given in the literature for 2,4-dimethylhydrocinnamic acid were 106 and 111.5°[15].

0.3923 g sub.: 19.7 ml 0.0927 N KOH. Found: M 184.6. $C_{11}H_{14}O_2$. Calculated: M 178.

Acrylonitrile–chlorobenzene. 6.8 g of acrylonitrile, 29 g of benzene and 56.3 g of $AlCl_3$ were used. The molar ratio was 1:2:3.2. The mixture was heated for 30 hours at 140-165°. 2.5 g (12%) of the nitrile of o-chlorohydrocinnamic acid (II) was obtained:

B.p. 147-152° at 15 mm, n_D^{20} 1.5475, d_4^{20} 1.1706, MR_D 44.86; calculated 44.85.

On saponification with 50% H_2SO_4, o-chlorohydrocinnamic acid having a m.p. of 96-97° [15] was obtained, and it produced no depression of the melting point when mixed with o-chlorohydrocinnamic acid obtained by the condensation of β-chloropropionitrile with chlorobenzene.

Condensation of acrylonitrile with benzene. To a solution of 6.8 g (0.13 mole) of acrylonitrile in 29 g (0.37 mole) of benzene, 47.7 g (0.36 mole) of $AlCl_3$ was gradually added. The mixture was heated on the water bath until all the $AlCl_3$ and the precipitated complex were dissolved, then it was quickly poured into an autoclave and heated for 10 hours, at 150-160°. After the usual treatment of the reaction mixture, 4.5 g (27%) of the nitrile of hydrocinnamic acid (I) was obtained:

B.p. 128-130°, at 16 mm, n_D^{20} 1.5228, d_4^{20} 1.0015, MR_D 39.9; calculated 39.9.

Saponification with NaOH in the presence of hydrogen peroxide yielded the amide, having a m.p. of 105-106° whereas the highest melting point given in the literature was 105° [16].

Condensation of the nitrile of cinnamic acid with benzene. To a solution of 6.4 g (0.05 mole) of the nitrile of cinnamic acid, which was obtained from acrylonitrile and phenyldiazonium chloride [17], in 35 g (0.45 mole) of benzene, 10 g (0.075 mole) of $AlCl_3$ was added. The mixture was heated for 5 hours at 80°. After the usual treatment of the mixture, 8.9 g (93%) of the nitrile of β,β-diphenylpropionic acid (VII) was obtained:

B.p. 181-183° at 5 mm; 163-165° at 2 mm; m.p. 88-89°. According to data in the literature, the m.p. is 100° [15]. In spite of repeated recrystallization from petroleum ether and alcohol, we did not succeed in raising the melting point.

Production of β,β-diphenylpropionic acid and its amide. A solution of 1.8 g (0.0087 mole) of nitrile (VII) and 1.8 g (0.033 mole) of KOH in 9 ml of alcohol was boiled for 2 hours. Strong evolution of NH_3 was observed. The crystals precipitating, after dilution with water and cooling were washed with water, dried and recrystallized from benzene. In this way, the amide with m.p. of 126-127° was obtained. According to data in the literature, the m.p. is 127° [15].

Found %: N 6.21. $C_{15}H_{15}NO$. Calculated %: N 6.20.

β,β-Diphenylpropionic acid was precipitated from the alkaline filtrate after it was acidified and concentrated to a small volume. The acid crystallized from dilute alcohol in the form of large, thick needles, m.p. 154-155°. According to data in the literature, the m.p. was 154-155° [15].

Production of the nitrile of γ,γ,γ-trichlorocrotonic acid (V). 124 ml of pyridine was mixed, with cooling, with 39.5 g (0.47 mole) of cyanoacetic acid. To the solution obtained, 100 g (0.7 mole) of chloral was added from a dropping funnel at such a rate that the flask was only slightly warm. After 40 minutes the evolution of CO_2 began. After addition of all of the chloral the mixture stood for 12 hours, and then was stirred for 2 hours at room temperature, and for 1 hour at the water bath temperature, until the evolution of CO_2 ceased. The pyridine was washed off with 20% H_2SO_4, and the product was extracted several times with ether. The ether extract was washed with water and dried over calcined Na_2SO_4. After removal of the ether, the residuals were fractionally distilled in vacuo. 20.6 g of nitrile (V) was obtained:

B.p. 96-97° at 38 mm, 121-123° at 90 mm, n_D^{20} 1.5027, d_4^{20} 1.4160, MR_D 35.57; calculated 34.57.

3.225 mg sub.: 3.327 mg CO_2; 0.450 mg H_2O. 7.820 mg sub.: 0.659 ml N_2 (32°, 709 mm). 0.2083 g sub.: 0.5222 g AgCl. Found %: C 28.15; H 1.56; N 8.7; Cl 62.02. $C_4H_2Cl_3N$. Calculated %: C 28.15; H 1.17; N 8.2; Cl 62.46. Nitrile of γ,γ,γ-trichlorocrotonic acid is not described in the literature.

On saponification of nitrile (V) with an alcoholic solution of KOH, fumaric acid, m.p. 280°, was obtained, and produced no depression of the melting point when mixed with known fumaric acid.

Condensation of the Nitrile of γ,γ,γ-Trichlorocrotonic Acid with Benzene

A solution of 6 g (0.035 mole) of nitrile (V) in 35 g (0.45 mole) of benzene, after addition of 5.6 g (0.042 mole) of $AlCl_3$, was heated on the water bath for 5 hours at 65-70°. 4.7 g (63%) of the nitrile of β-phenyl-γ,γ-dichlorovinylacetic acid (VI) was obtained:

B.p. 122° at 3 mm, n_D^{20} 1.5585, d_4^{20} 1.2553, MR_D 54.48; calculated 53.86.

3.661 mg sub.: 7.460 mg CO_2; 1.065 mg H_2O. 6.25 mg sub.: 0.343 ml N_2 (16°, 734 mm). 0.1166 g sub.: 0.1558 g AgCl. Found %: C 55.68; H 3.26 N 6.26; Cl 33.01. $C_{10}H_7NCl_2$. Calculated %: C 56.60; H 3.29; N 6.58; Cl 33.41.

Phenylsuccinic acid. 2.1 g of nitrile (VI) was boiled for 24 hours with 20 ml of 20% KOH. After acidification, a precipitate came down, and from it an acid, m.p. 165-166° (from a mixture of benzene and alcohol), was extracted by ether. The sample, when mixed with phenylsuccinic acid, which we obtained by the method of [18], produced no m.p. depression.

SUMMARY

1. It was found that acrylonitrile cyanoethylates benzene and chlorobenzene in the presence of $AlCl_3$ only at 140-180°, which is accounted for by the passivating effect that complex formation at the nitrile group had on the activity of the double bond of acrylonitrile. Mesitylene and o-xylene entered into this reaction more readily than did benzene.

2. The CCl_3- and C_6H_5-groups in α,β-unsaturated nitriles increased the reactivity of the double bond. The nitrile of cinnamic acid reacted with benzene in the presence of 1.6 moles of $AlCl_3$, giving the nitrile of β,β-diphenylpropionic acid in a yield of 93%. The nitrile of γ,γ,γ-trichlorocrotonic acid, under the influence of 1.2 moles of $AlCl_3$, added to benzene, giving the nitrile of β-phenyl-γ,γ-dichlorovinylacetic acid in a yield of 63%.

3. By condensation of β-chloropropionitrile with benzene and chlorobenzene in the presence of $AlCl_3$, the nitriles of β-phenylpropionic and β-chlorophenylpropionic acids were obtained in a yield of 66-69%.

4. It was found that the formation of a stable complex with $AlCl_3$ inhibited the addition of HCl at the double bond of acrylonitrile.

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USE OF PARALDEHYDE IN THE GRIGNARD REACTION

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It is well known that aldehydes are usually used for the synthesis of secondary alcohols, according to Grignard but operation with the lower aldehydes, particularly acetaldehyde, is accompanied by a number of disadvantages caused by their low boiling points. In this connection, we were faced with the problem of replacing acetaldehyde in the Grignard reaction with its polymer — paraldehyde, which is easily obtained, boils much higher than acetaldehyde, and, therefore, is much more convenient to use. Such a substitution of a polymer for a monomer in the Grignard reaction was accomplished long ago, for example, for paraform, which was used in place of gaseous formaldehyde.

Checking the literature with respect to this problem, it should be pointed out that until January 1, 1948 only a single Grignard synthesis involving the use of paraldehyde had been described [1]. Also in the subsequent literature we found no Grignard syntheses employing paraldehyde. It seems to us that the "neglect" of paraldehyde may be explained by the fact that, in the work cited above, the alcohol was obtained in a much smaller yield [2] that when acetaldehyde was employed in the same reaction [3]. However, it seems to us that such a neglect of paraldehyde is hardly warranted, since the yield of the corresponding alcohol might be increased by changing the conditions, and as a result of this we undertook the present work; thus, we devoted our attention not only to the alcohol which should be obtained, but also to the substances forming with it during the reaction. We wanted to observe the latter, since until the present time, with few exceptions, no substance, other than the alcohol forming during the reaction between acetaldehyde and the Grignard complex, had been investigated. Meanwhile, many opinions might be given concerning the mechanism of the Grignard reaction, which forms substances simultaneously with the alcohol.

In our work, we investigated the reaction of paraldehyde with magnesium-organic compounds obtained from methyl iodide, ethyl iodide, ethyl bromide, propyl bromide, isopropyl bromide, butyl and isobutyl bromides, cyclohexyl chloride, bromobenzene, benzyl chloride and allyl bromide, and observed the reaction of paraldehyde with the Iotsich complex.

At first, syntheses were carried out under the usual conditions of the Grignard synthesis, i.e., in an ether medium, with cooling, followed by 2-3 hours of heating of the reaction mixture on a water bath. Since the yields of the corresponding alcohols under these conditions were small, we increased the heating times to 8 hours, and even to 12-14 hours; in this way, the alcohol yields were increased. In individual cases, in order to obtain a more complete consumption of the magnesium-organic compound, the latter was heated with a benzene solution of paraldehyde, after which the benzene, like the ether, was removed. In this case, the reaction mixture could be heated to 80°, which led to a considerable increase of the alcohol yields. Because the procedure and conditions for carrying out the reaction are generally known, we discuss the experimental part briefly. For the same reason, with few exceptions, we present no detailed description of all the substances investigated, although they were analyzed. Let us point out that each experiment was carried out 3-4 times under the same conditions, and the results agreed in all cases.

As shown by the investigation, the alcohol yields depended to a great extent on the conditions of heating; prolonged heating in an ether medium often increased the alcohol yield 2-fold. In some cases, the presence of alcohol was not detected after heating for 3 hours, but all of the alcohols were obtained after prolonged heating of paraldehyde with the Grignard complex in an ether medium. However, prolonged heating in ether medium did not always give satisfactory results. In these cases, heating was carried out in a benzene medium, which enabled us to obtain the alcohol even when it seemed that paraldehyde and the magnesium-organic compound would not react. The results of the experiments are recorded in Tables 1 and 2.

The formation of hydrocarbons during these reactions, as is known, resulted from the simultaneous occurrence of the Würtz reaction. We can account for the formation of ketones by the oxidizing action of the excess paraldehyde which in this way was reduced to ethyl alcohol [4].

We accounted for the formation of p-ethylphenol by the partial rearrangement of methylphenylcarbinol, which occurs on heating the carbinol in a benzene medium:

TABLE 1

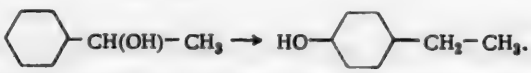
Relation of Alcohol Yields to Heating Conditions

Name of alcohol	Alcohol yield based on quantity of paraldehyde consumed			Characteristics of the alcohol obtained					
	on heating in ether medium		in benzene medium	boiling point	n_D^{20}	d_4^{20}	% OH found	% OH calc'd	literature
	2-3 hrs	8-14 hrs							
Dimethylcarbinol	23	41	–	80-85°	1.374	0.78	28.17	28.33	[11]
Methylethylcarbinol	21	50	–	99-100	–	0.810	–	–	[10]
Methylpropylcarbinol	17	23	–	118-120	1.413	0.810	19.23	19.32	[12]
Methylisopropylcarbinol	16	25	–	112-116	1.398	0.820	19.58	19.32	[12]
Methylbutylcarbinol	0	17	32	136-140	1.413	0.820	16.82	16.66	[12]
Methylisobutylcarbinol	0	0	16	55 (30 mm)	1.411	0.815	determined %C & H the same		[12]
Methylallylcarbinol	15	30	–	110-116	1.425	0.8302			[12]
Methylphenylcarbinol	0	31.4	–	78 (5 mm)	1.522	1.014	14.11	13.93	[12]
Methylcyclohexylcarbinol	0	21	38	83 (13 mm)	1.463	0.925	13.00	13.28	[12]
Methylbenzylcarbinol	34	39	–	212	1.520	0.990	12.34	12.60	[12]
Hexine-3-diol-2,5	0	0	22.4	122-123 (12 mm)			29.90	29.82	[15]

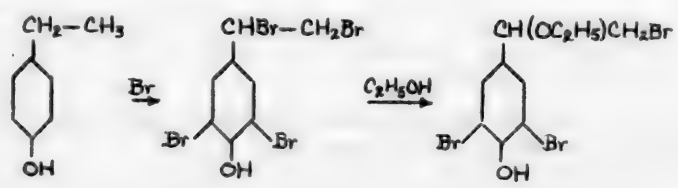
TABLE 2

Substances Obtained (Besides the Alcohols) by the Reaction of Paraldehyde with RMgX

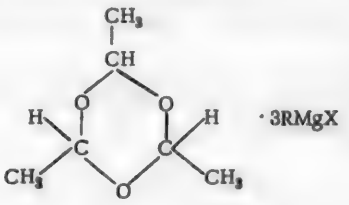
RMgX	Medium in which the reaction was carried out	Substance obtained	Yield (%)	Characteristics of the compound obtained
CH_3MgI	Ether	CH_3COCH_3	16.0	Semicarbazone m.p. 190° [10]
C_2H_5MgBr	Ether	$CH_3COC_2H_5$	55.2	Semicarbazone m.p. 136.5° [10]
C_2H_5MgI	Ether	The same	28.0	The same
C_3H_7MgBr	Ether	C_6H_{14}	12.0	B.p. 68-70°, n_D^{20} 1.375
		$CH_3COC_4H_9$	14.0	Semicarbazone m.p. 110° [12]
$(CH_3)_2CHMgBr$	Ether	$(CH_3)_2CHCH(CH_3)_2$	9.5	n_D^{20} 1.373, d_4^{20} 0.820 [12]
		$CH_3COCH(CH_3)_2$	25.0	–
$n\text{-}C_4H_9MgBr$	Ether, benzene	C_6H_{12}	12.0	n_D^{20} 1.3828, d_4^{20} 0.68 [12]
$(CH_3)_2CHCH_2MgBr$	Benzene	$CH_3CH[OCH(CH_3)C_4H_9\text{-iso}]_2$	37.0	B.p. 83-86° (5 mm), n_D^{20} 1.454, d_4^{20} 0.887 Found %: C 73.76; H 12.98 Calculated %: C 73.04; H 13.04
$H_2C{=}CH{-}CH_2MgBr$	Ether: 2-3 parts	$H_2C{=}CH(CH)_2CH_2{=}CH_2$	47	n_D^{20} 1.401, d_4^{20} 0.688 [12, 13]
	10 parts	The same	29.4	
$BrMgC{\equiv}CMgBr$	Benzene	$CH_3CH(OH)C{\equiv}CH$	7.0	Correspond to literature data [15]
$C_6H_{11}MgCl$	Ether, benzene	Cyclohexene and cyclohexyl chloride		B.p., d_4^{20} and n_D^{20} correspond to literature data [12]
C_6H_5MgBr	Ether	$C_6H_5C_6H_5$	15.3	M.p., corresponds to literature data [12, 14]
		$p\text{-}HOC_6H_4(C_2H_5)$	14.0	
$C_6H_5CH_2MgCl$	Ether	$C_6H_5CH_3$	48.0	B.p. 110°, n_D^{20} 1.495
		$C_6H_5CH_2CH_2C_6H_5$	18.0	M.p. 52-53° without depression with known substance [12]



By the action of bromine water, and subsequent recrystallization from alcohol, p-ethylphenol underwent the following transformations [14]:

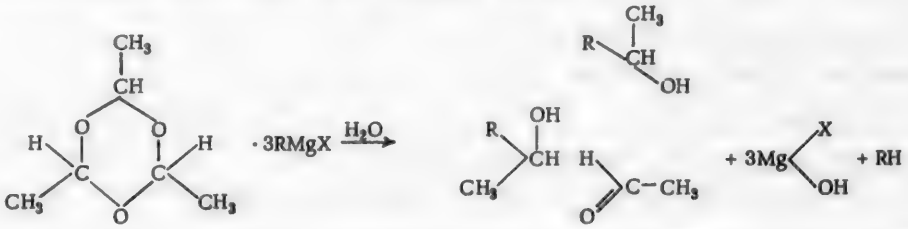


At first we accounted for the small yields of alcohol, obtained under conditions involving the brief heating of paraldehyde with the Grignard complex, exclusively on the basis of the slow depolymerization of paraldehyde. However, such an assumption was refuted by the following observations. In the reactions of paraldehyde with different RMgX, after a certain length of time (depending on the R radical), the reaction of Michler's ketone [5] for the free magnesium-organic compound was negative, which indicated the absence of RMgX in the reaction mixture, but after decomposition of the reaction products with water we found paraldehyde and also hydrocarbons corresponding to the radical of the magnesium-organic compound. Under conditions in which 1 mole of paraldehyde to 3 moles of RMgX was used, the absence of free magnesium-organic compound in the reaction mixture some time after the beginning of the reaction, and the later appearance of paraldehyde and hydrocarbon on treatment with water were accounted for by the fact that, initially, the RMgX adds to paraldehyde with the formation of an intermediate complex, due to the oxygen atoms of paraldehyde (A).

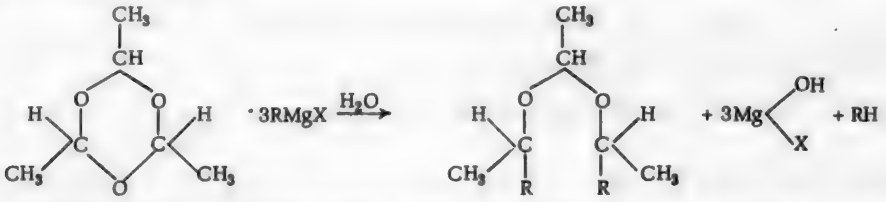


(A)

Then, depending on the conditions, either alcohol or hydrocarbon + paraldehyde is formed from this complex. In all probability, a non-uniform RMgX adds readily to paraldehyde. Those possessing an R of low molecular weight add more readily. However, because of steric hindrance, the addition of the triple molecules C_6H_5MgBr, $C_6H_5CH_2MgCl$, and in general, RMgX with an R of high molecular weight, is prevented. It is necessary to account for this by the fact that, on decomposition of the complex of paraldehyde with the RMgX cited above, acetaldehyde also was present in the reaction mixture, but this was not observed for R = CH_3–, C_2H_5–, C_3H_7–, etc.. In these cases, the decomposition of the complex may be represented as follows:



Assuming the presence of the above-mentioned complex, it is not difficult to account for the formation of acetal in one of the experiments (Table 2):



The formation of similar acetals was observed during the reaction of paraform with C_3H_7MgBr [6], C_4H_9MgBr [7], $C_5H_{11}MgBr$ [8] and $C_6H_{11}MgBr$ [9].

EXPERIMENTAL

The paraldehyde, and also the benzyl chloride, bromobenzene, and allyl-, n-butyl and n-propyl bromides were "Kahlbaum", c.p. grade. The remaining alkyl halides were synthesized from alcohols. All the alkyl and aryl halides were distilled before use. For the reaction we used: 3 moles of alkyl (aryl) halide and 3 moles of magnesium to 1 mole of paraldehyde.

The fractions obtained from the distillation of the products from the reactions with paraldehyde in ether medium (on brief, as well as on prolonged heating), did not vary qualitatively; only their percentage contents changed. The unreacted paraldehyde was determined by its constants and by its depolymerization to acetaldehyde.

SUMMARY

1. Paraldehyde, like acetaldehyde, reacted with different magnesium-organic compounds of the aliphatic and aromatic series, with the formation of the corresponding secondary alcohols.

2. The alcohol yields depended on the nature of the radical of the magnesium-organic compound and on the length of time the reactants were heated in the ether medium. Other conditions being equal, as the number of carbon atoms in the radical increased, the yield of the corresponding alcohol decreased. Prolonged heating (10-12 hours) in ether medium increased the alcohol yields.

3. Replacement of the ether medium by benzene, making it possible to heat the reaction mixture to 70-80°, increased the yield of the corresponding alcohols considerably, and also enabled us to obtain the latter in instances when they would not have been obtained under the usual conditions (ether medium).

4. Ketones and hydrocarbons were obtained as by-products of the Grignard reaction with paraldehyde, and the formation of acetals was also observed.

5. We proposed a probable scheme for the reaction, assuming the formation of a complex compound of paraldehyde with the magnesium-organic compound.

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REACTIONS OF METAL HALIDE-ALCOHOLATES

I. REACTION OF MAGNESIUM HALIDE-DIARYLCARBINOL ALCOHOLATES WITH ESTERS

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A study of the reaction of magnesium halide-alcoholates with esters, chiefly with ethyl acetate, was made by G. L. Stadnikov [1].

He investigated the reactions of the magnesium iodide-alcoholates of benzhydrol, β-methylcyclohexanol and menthol with ethyl acetate, used in double quantity in the reaction, and obtained the acetates of these alcohols. He also found that, in addition to benzhydryl acetate, under certain conditions, dibenzhydryl ether and benzhydryl ethyl ether formed.

Work concerning the formation of esters by the action of ethyl acetate on magnesium bromide-ethylphenylcarbinolate, and also on magnesium bromide-benzhydrolate, was recorded by A. N. Nesmeyanov and V. A. Sazonova [2]. The action of esters on the mixed magnesium alcoholates was also studied by D. Ivanow and T. Roustche [3], who found that when the alcoholate radical is heavier than the ester group radical, the latter replaces the former.

The present work was undertaken for the purpose of studying the effect of the structure of the esters on the character of their reactions with mixed magnesium diarylcarbinolates, and for the purpose of studying the effect of the structure of the diarylcarbinols on the nature of the reactions of mixed magnesium alcoholates with esters.

In contrast with the work of other authors, we carried out the reaction using only equimolecular quantities of reactants, in order to get a clearer picture of these effects.

As shown by the investigations, from the reaction of the magnesium halide-carbinolates of the unsubstituted and mono-ortho-substituted diarylcarbinols with ethyl formate, the chief, and more often the only reaction product, was a diarylmethane halide, R_2CHX. In some cases we isolated the ethers of the carbinols, $R_2CH-O-CHR_2$, for which the composition of the reaction products depended on the structures of the aryl radicals, as well as on the nature of the halide. The reaction of the magnesium halide-carbinolates of the di-ortho-substituted diarylcarbinols with the ethyl formate is of a different nature. These reactions led to the formation of hydrocarbons – diarylmethanes.

The experimental results are recorded in Table 1.

TABLE 1

No.	Reactants (1:1)	Composition of reaction products (%)		
		halide	carbinol	ether
1	MgCl-benzhydrolate + ethyl formate	61	17	22
2	MgBr-benzhydrolate + ethyl formate	100	–	–
3	MgCl-di-p-tolylcarbinolate + ethyl formate	33	67	–
4	MgBr-di-p-tolylcarbinolate + ethyl formate	60	40	–
5	MgCl-di-o-tolylcarbinolate + ethyl formate	90	10	–
6	MgBr-di-o-tolylcarbinolate + ethyl formate	100	–	–
7	MgCl-di-α-naphthylcarbinolate + ethyl formate	100	–	–
8	MgBr-di-α-naphthylcarbinolate + ethyl formate	100	–	–
9	MgCl-dimesitylcarbinolate + ethyl formate	–	–	–*
10	MgBr-dimesitylcarbinolate + ethyl formate	–	–	–*

The rule resulting from the data of Table 1 is explicit: the yield of diarylmethane halide increases with an increase of the electronegativity of the aryl radical, and therefore, with an increase of the mobility of the hydroxyl group.

* 100% dimesitylmethane.

The structure of the ester also influences the nature of the reaction of the magnesium halide-carbinolates with esters. From the data of Table 2 it is obvious that a decrease of the dissociation constants of the acids from which the esters were formed has a great effect on the nature of the products obtained. If diethyl oxalate is completely converted to benzhydryl bromide by magnesium bromide-benzhydrolate, then diethyl succinate is almost completely converted to dibenzhydryl ether by the same alcoholate.

TABLE 2

No.	Reactants (1:1)	Composition of the reaction products (%)		
		benzhydryl halide	benzhydrol	dibenzhydryl ether
1	MgBr-benzhydrolate + diethyl succinate	9	–	91
2	MgBr-benzhydrolate + diethyl malonate	21	–	79
3	MgBr-benzhydrolate + diethyl oxalate	100	–	–
4	MgBr-benzhydrolate + diethyl sulfate.	4	–	96
5	MgBr-benzhydrolate + ethyl benzoate	–	98	2
6	MgBr-benzhydrolate + ethyl acetate	1.5	98.5	–
7	MgCl-benzhydrolate + ethyl acetate	0.2	99.8	–

We wish to point out that, although the dissociation constant of benzoic acid (k_{25} $6.6 \cdot 10^{-5}$) is almost equal to the 1st dissociation constant of succinic acid (k_{25} $6.4 \cdot 10^{-5}$), its ester shows hardly any activity toward the magnesium halide-carbinolates.

The results of the investigation enabled us to understand the reaction between the aryl magnesium halides and the formates, and also to understand the source of the anomalies occurring in this reaction [4-8].

EXPERIMENTAL

The general conditions for carrying out reactions between the magnesium halide-alcoholates of the diarylcarbinols and esters are as follows. To a diarylcarbinol dissolved in a triple volume of anhydrous ether, we added an ether (3 volumes) solution of the magnesium-organic compound, which had been freed of an excess of magnesium (n-butyl magnesium chloride for preparation of the magnesium chloride-alcoholates and ethyl magnesium bromide for preparation of magnesium bromide-alcoholates).

To the ether solution of the magnesium halide-alcoholate we added an equimolecular quantity of the ester dissolved in an equal volume of anhydrous ether. The reaction mixture was heated for 3 hours, and then decomposed with 10% acetic acid solution and water. The ether layer was washed with a 10% solution of sodium bicarbonate, and then with water, until a neutral reaction was obtained. When ethyl oxalate was used for the reaction, we observed the separation of magnesium oxalate in the ether layer, and its precipitation in the aqueous layer. The ether solution was dried over calcined sodium sulfate, the solvent was removed and the product, after vacuum distillation was studied.

1. The reaction of magnesium chloride-benzhydrolate with ethyl formate. The reactants were: 12.3 g of benzhydrol, 6.2 g of butyl chloride, 2 g of magnesium and 5.0 g of ethyl formate. The reaction conditions are given below.

On vacuum distillation (5 mm) of the reaction products, the following fractions were obtained: 1st, 123-150°, 10.0 g; 2nd, 180-200°, 2.7 g; residue in flask – 1.0 g.

Treatment of a weighed portion of the 1st fraction with a saturated alcoholic solution of silver nitrate, and heating [9], gave a chlorine content of 13.70% (17.49% calculated for benzhydryl chloride).

Thus, the 1st fraction contained 78.3% of benzhydryl chloride, and 21.7% of benzhydrol (or on conversion to total products obtained, and by rounding off the figures to whole numbers, 61 and 17%).

By repeated distillation, the 1st fraction was separated into two equal portions. From the first half, fractional recrystallization from petroleum ether yielded benzhydryl chloride with a m.p. of 11°.

Found %: Cl 17.10. $C_{13}H_{11}Cl$. Calculated %: Cl 17.49.

According to data in the literature [10], benzhydryl chloride has a m.p. of 14°.

Fractional recrystallization from the same solvent yielded benzhydrol, with a m.p. of 68°, from the second half of the fraction.

A m.p. of 67.5-68° is cited in the literature [11] for this substance. A test sample of the substance, when mixed with synthetic benzhydrol, produced no m.p. depression.

The 2nd fraction was recrystallized twice from petroleum ether. Dibenzhydryl ether with a m.p. of 106-107° was isolated.

In the literature [12], a m.p. of 109-110° is given for this compound.

Found %: C 88.90; H 6.29. $C_{26}H_{22}O$. Calculated %: C 89.11; H 6.33.

The yield of dibenzhydryl ether was 3.7 g (22%), since after the removal of the reaction products, the residue (1.0 g) in the flask also consisted of this ether.

2. The reaction of magnesium bromide-benzhydrolate with ethyl formate. For the reaction we used: 12.3 g of benzhydrol, 7.3 g of ethyl bromide, 2 g of magnesium and 5.0 g of ethyl formate. Vacuum distillation of the reaction product yielded 15 g of benzhydryl bromide with a b.p. of 151-153° (6 mm); m.p. 37-38° (from petroleum ether).

Found, (Stepanov) bromine 31.96%. $C_{13}H_{11}Br$. Calculated %: Br 32.39.

A m.p. of 45° was given in the literature [13] for the bromide.

Thus, under the conditions employed, all the benzhydrol was converted to benzhydryl bromide.

3. The reaction of magnesium chloride-di-p-tolylcarbinolate with ethyl formate. We used: 14 g of di-p-tolylcarbinol, 6.2 g of butyl chloride, 2 g of magnesium and 5.0 g of ethyl formate. The reaction product distilled in vacuo at 6 mm in the range of 140-160° (13 g). The di-p-tolylchloromethane content was determined by a saturated solution of silver nitrate, as denoted in experiment 1.

Found %: Cl 5.15. $C_{15}H_{15}Cl$. Calculated %: Cl 15.37.

Thus, the di-p-tolylchloromethane content in the reaction product was 33%, and the carbinol content was 67%. No benzhydrylformic ether was found in the reaction products.

4. The reaction of magnesium bromide-di-p-tolylcarbinolate with ethyl formate. For the reaction we used 14 g of di-p-tolylcarbinol, 7.3 g of ethyl bromide, 2 g of magnesium and 5.0 g of ethyl formate. All of the reaction product distilled in vacuo at 5 mm in the range 142-165° (13.5 g). The bromine content was determined by means of silver nitrate.

Found %: Br 17.42. $C_{15}H_{15}Br$. Calculated %: Br 29.04.

Consequently, the bromide content in the reaction products was 60%. The formate of this carbinol was not observed in the reaction products.

5. The reaction of magnesium chloride-di-o-tolylcarbinolate with ethyl formate. For the reaction, we used the same weights of reactants as were used in experiment 3, except that we used di-o-tolylcarbinol instead of di-p-tolylcarbinol. 13.6 g of a substance with a b.p. of 138-150° (4 mm) was obtained.

The chlorine content in the mixture of products obtained was 13.73%. Calculated for di-o-tolylchloromethane it was 15.37%.

The di-o-tolylchloromethane content in the reaction products was 90%, the unreacted carbinol content was 10%.

The di-o-tolylchloromethane, separated after 2 recrystallizations from petroleum ether, had a m.p. of 70-71°.

Found %: Cl 15.12. $C_{15}H_{15}Cl$. Calculated %: Cl 15.37.

According to the literature [14], this substance has a m.p. of 70°.

6. The reaction of magnesium bromide-di-o-tolylcarbinolate with ethyl formate. The reaction was carried out using the same weights of reactants as were used in experiment 4. Di-o-tolylcarbinol was used instead of di-p-tolylcarbinol.

The reaction product distilled at 142-144° (4 mm).

Found %: Br 28.70. $C_{15}H_{15}Br$. Calculated %: Br 29.04.

The bromine content of this product was indicated by the fact that all of the di-o-tolylcarbinol was converted to di-o-tolylbromomethane. The di-o-tolylbromethane obtained after one recrystallization from petroleum ether melted at 66-67°. This bromide was not described in the literature.

7. The reaction of magnesium chloride-di-α-naphthylcarbinolate with ethyl formate. For the reaction we used 9.5 g of di-α-naphthylcarbinol, 3.1 g of butyl chloride, 1 g of magnesium and 2.5 g of ethyl formate. After removal of the ether, the reaction product did not distil because of its high boiling point. The chlorine content of the non-purified di-α-naphthylchloromethane was 10.9%. The chloride had a m.p. of 180-181° after two recrystallizations from toluene.

Found %: Cl 11.48. $C_{21}H_{15}Cl$. Calculated %: Cl 11.71.

In the literature [15], a m.p. of 188-189° is given for di-α-naphthylchloromethane.

8. The reaction of magnesium bromide-di-α-naphthylcarbinolate with ethyl formate. The reactants were: 9.5 g of di-α-naphthylcarbinol, 3.7 g of ethyl bromide, 1 g of magnesium and 2.5 g of ethyl formate.

On decomposition of the reaction mixture with water and acetic acid, the precipitate of di-α-naphthylbromomethane, which was difficultly soluble in hydrous ether, was separated, and after drying, it melted at 173-175° (the Br content was 22.1%). The di-α-naphthylbromomethane had a m.p. of 181-182° after purification by recrystallization from toluene.

Found %: Br 22.70. $C_{21}H_{15}Br$. Calculated %: Br 23.01.

9. The reaction of magnesium chloride-dimesitylcarbinolate with ethyl formate. For the reaction we used 9.0 g of dimesitylcarbinol, 3.1 g of butyl chloride, 1 g of magnesium and 2.5 g of ethyl formate.

Vacuum distillation of the substance obtained, followed by 2 recrystallizations from petroleum ether, gave dimesitylmethane with a m.p. of 130°. A test sample, mixed with dimesitylmethane obtained by the reaction of mesityl magnesium bromide with ethyl formate, produced no reduction of the melting point.

Found %: C 90.25; H 9.15. $C_{19}H_{24}$. Calculated %: C 90.41; H 9.59.

In the literature [16], a m.p. of 134-135° is indicated for this hydrocarbon.

10. The reaction of magnesium bromide-dimesitylcarbinolate with ethyl formate. The results of the reaction of the magnesium bromide-alcoholate of dimesitylcarbinol with ethyl formate were similar to those of the preceding reaction. Dimesitylmethane, with a m.p. of 130° was the only reaction product.

11. The reaction of magnesium bromide-benzhydrolate with diethyl succinate. The reactants were: 9.2 g of benzhydrol, 5.5 g of ethyl bromide, 2 g of magnesium and 8.7 g of ethyl succinate. By vacuum distillation of the reaction product at 6 mm the following fractions were obtained: 1st, 85-130°, 1.9 g; 2nd, 130-250°, 6.2 g; residue, 2 g.

The 1st fraction consisted of diethyl succinate. An analysis of the 2nd fraction showed a bromine content of 3.77%, which corresponded to 11.7% benzhydryl bromide content. On conversion to the total product, including the residue (2 g), the yield of benzhydryl bromide was 9%. The fact that the hydroxyl group was not observed in the substance indicated the absence of benzhydrol.

The 2nd fraction, on redistillation, distilled completely at 225-230° (6 mm). On recrystallization from petroleum ether, dibenzhydryl ether with a m.p. of 107° was obtained.

In the literature [17], a m.p. of 109° was indicated for this substance.

Found %: C 88.87; H 6.28. $C_{26}H_{22}O$. Calculated %: C 89.11; H 6.33.

The content of dibenzhydryl ether in the reaction product was 91%.

12. The reaction of magnesium bromide-benzhydrolate with diethyl malonate. The reactants were used in quantities of 1/20 mole. On vacuum distillation of the reaction product at 3.5 mm, the following fractions were obtained: 1st, 80-90°, 3.0 g; 2nd, 130-240°, 7.5 g; residue 1 g.

The 1st fraction consisted of ethyl malonate.

The 2nd fraction, containing 7.7% bromine was distilled a second time. The main volume of the product distilled at 210-225° (4.5 mm), and after recrystallization from petroleum ether, dibenzhydryl ether with a m.p. of 107° was recovered. Since benzhydrol was not observed in the reaction products, the benzhydryl bromide and dibenzhydryl ether contents in the reaction mixture were 21 and 79%, respectively.

13. The reaction of magnesium bromide-benzhydrolate with diethyl oxalate. The same quantities (1/20 mole) of reactants were used. On vacuum distillation of the reaction product at 4.5 mm, the following fractions were obtained: 1st, 60-120°, 3.5 g; 2nd, 147-155°, 8.0 g; residue, 0.5 g.

Determination of bromine in the product from the 2nd fraction (30.7%) showed that it consisted entirely of benzhydryl bromide. The benzhydryl bromide, recrystallized from petroleum ether, melted at 38°.

Found %: Br 32.10. Calculated %: Br 32.39. In the literature [13], a m.p. of 45° is given for benzhydryl bromide.

No benzhydrol was observed in the reaction products.

14. The reaction of magnesium bromide-benzhydrolate with diethyl sulfate. The reactants were used in the same quantities as in the preceding experiments (1/20 mole). Vacuum distillation gave the following fractions: 1st, 70-75° (4 mm), 2.0 g; 2nd, 200-220° (4 mm), 7.5 g; residue, 1 g.

From the bromine content in the product from the 2nd fraction (1.36% bromine), the benzhydryl bromide content was found to equal 3.7%. Since no benzhydrol was observed in the reaction product, the yield of dibenzhydryl ether was 96.3%. After a single recrystallization from petroleum ether, the dibenzhydryl ether had a m.p. of 106°.

15. The reaction of magnesium bromide-benzhydrolate with ethyl benzoate. The same quantities (1/20 mole) of reactants were used.

The synthesized substance was vacuum distilled. The fractions obtained were: 1st, 90-105°, 5 g; 2nd, 130-150°, 8.0 g; residue, 0.5 g.

The 1st fraction consisted of ethyl benzoate..

No halide was found in the products from the 2nd fraction. The substance from the 2nd fraction melted at 68° after recrystallization from petroleum ether. A mixture of the test sample and original benzhydrol showed no m.p. depression. Therefore, this fraction consisted of benzhydrol.

The residue (0.5 g) in the flask was recrystallized from the same solvent. 0.2 g (2%) of dibenzhydryl ether was separated; the m.p. was 106°.

16. The reaction of magnesium bromide- and magnesium chloride-benzhydrolates with ethyl acetate. Application of the same method of investigation showed that ethyl acetate, only to a small degree, converted magnesium halide-benzhydrolate to benzhydryl halide. We found 0.2% benzhydryl chloride in the 1st reaction, and 1.5% benzhydryl bromide in the 2nd reaction. No benzhydryl acetate was found.

SUMMARY

1. A new method, based on the reaction of magnesium halide-diarylcarbinolates with ethyl formate and ethyl oxalate, was proposed for the synthesis of diarylhalomethanes.

2. A new method, based on the reaction of the di-ortho-substituted magnesium halide-diarylcarbinolates with ethyl formate, was proposed for the reduction of the di-ortho-substituted diarylcarbinols to the diarylmethanes.

3. It was found that a depression of the dissociation constant of the acid from which the ester was formed had a substantial effect on its reaction with the magnesium halide-diarylcarbinolates.

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SYNTHESIS AND HYDROGENATION OF 2,4,7,9-TETRAMETHYLDECINE-5-TETRAOL-2,4,7,9

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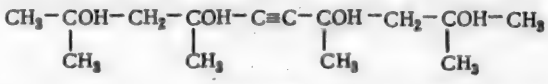
Since only a few acetylenic monoatomic alcohols [1] are known, the purpose of our work was to synthesize an acetylenic monoatomic alcohol, and to study the nature of its hydrogenation in the presence of catalysts.

It is known from the literature [2] that an attempt to condense vinylacetylene with diacetone alcohol, in the presence of alkali, under the reaction conditions specified by A. E. Favorsky, leads to the cleavage of diacetone alcohol, forming acetone; the latter condenses with vinylacetylene, forming dimethylvinylacetylenecarbinol.

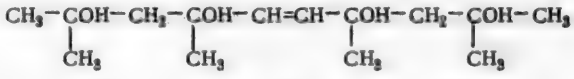
Our experiments showed that, under similar conditions, diacetone alcohol reacts with acetylene giving tetramethylbutinediol and dimethylacetylenecarbinol; therefore, we obtained a monoatomic alcohol by the magnesium-organic synthesis.

It was shown that diacetone alcohol and dimagnesium-dibromoacetylene form acetylenic erythritol as the two stereoisomers with a m.p. of 129-130° (I) and a b.p. of 99-104° at 7 mm (II).



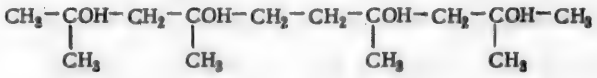
(I and II)

Hydrogenation of the crystalline isomer (I) in the presence of colloidal palladium showed the similarity of this erythritol to acetylene γ-glycol; after the addition of 2 atoms of hydrogen, only ethylenic erythritol with a m.p. of 91-92° (III) formed:



(III)

Saturated erythritol, with a m.p. of 95-97° (IV), was formed by addition of 4 atoms of hydrogen:



(IV)

It is known that the rate of hydrogenation of isomeric compounds is not uniform [3]. We showed that the isomeric erythritols which we obtained behaved similarly: the liquid isomer (II) hydrogenated more rapidly than did the crystalline isomer. We obtained the liquid, saturated erythritol, with a b.p. of 96-97° at 8 mm, by hydrogenation of the liquid isomer.

EXPERIMENTAL

Synthesis of Acetylenic Erythritol

To dimagnesium-dibromoacetylene, obtained from 24 g of magnesium and 110 g of ethyl bromide, we added dropwise 58 g of diacetone alcohol diluted to twice its volume with anhydrous ether, stirring and heating the mixture on a water bath at 40-50°. Stirring was continued for 2 hours after addition of the keto alcohol. Then the reaction mixture was allowed to stand 24 hours, then decomposed by 15% ammonium sulfate and 5% sulfuric acid. The ether layer and the ether extract were combined and dried with sodium sulfate. After the ether was removed, the oil partially crystallized. We obtained 17 g of crystals (from benzene) with a m.p. of 129-130° and 33 g of an oil. The oil was vacuum distilled at 7 mm: 1st fraction, 99-104°, 12 g; 2nd fraction, 163-170°, 10 g. The 2nd fraction crystallized (from benzene) and had a m.p. of 129-130°.

Analysis of Crystals with a M.p. of 129-130°

0.0966 g sub.: 0.2310 g CO_2; 0.0892 g H_2O. 0.0188 g sub.: 0.0936 g camphor: Δt 31°. 0.0108 g sub.: 3.8 ml CH_4 (17°, 735 mm). Found %: C 65.30; H 10.30. M 259.3. $C_{14}H_{22}(OH)_4$. Calculated %: C 65.14; H 10.07. M 258. 4.2 ml CH_4.

Analysis of Liquid Substance with a B.p. of 99-104° (7 mm)

d_{20}^{20} 0.9437, n_D^{20} 1.4630.

0.1326 g sub.: 0.3284 g CO_2; 0.1326 g H_2O. 0.0776 g sub.: 18.01 g benzene: Δt 0.85°. 0.0726 g sub.: 24.0 ml CH_4 (17°, 738 mm). Found %: C 64.38; H 10.57. M 257. 24.0 ml CH_4. $C_{14}H_{22}(OH)_4$. Calculated %: C 65.14; H 10.07. M 258. 25.4 ml CH_4.

Hydrogenation of Acetylenic Erythritol (m.p. 129-130°) to Ethylenic Erythritol

Colloidal palladium was prepared by the usual method [4]: 1 ml of solution contained 1 mg of palladium. The activity of the catalyst was checked by tetramethylbutinediol, 0.01 mole of which, with 3 mg of palladium, added a molecule of hydrogen during a period of 18 minutes.

The hydrogenation was carried out under the same conditions (18°, 728 mm).

Experiment 1. We used 2.580 g of erythritol (0.01 mole), 50 ml of C_2H_5OH, 3 mg of palladium, and 272 ml of H_2.

Every 3 minutes, the following quantities of hydrogen (in ml) were added: 48, 39, 36, 30, 30, 25, 24, 22.3, 18. A total of 272.3 ml was added in 27 minutes.

After treatment of the hydrogenation product, we obtained crystals (from toluene), with a m.p. of 91-92°, which decolorized bromine water and permanganate solution.

0.1176 g sub.: 0.2786 g CO_2; 0.1176 g H_2O. 0.0204 g sub.: 0.2234 g camphor: Δt 14°. 0.0398 g sub.: 14.8 ml CH_4 (19°, 737 mm). Found %: C 64.61; H 11.14. M 263. $C_{14}H_{24}(OH)_4$. Calculated %: C 64.61; H 10.76. M 260. 15.1 ml CH_4.

Hydrogenation of Acetylenic Erythritol (m.p. 129-130°) to Saturated Erythritol

Experiment 2. The experiment was repeated under the same conditions, using 5 mg of palladium, and every 12 minutes the following quantities (in ml) of hydrogen were added: 156, 113, 79, 56, 48, 30, 25, 19, 13, 2, 1.1. A total of 543 ml of hydrogen was added in 117 minutes.

The crystals obtained after treatment of the hydrogenation product melted at 95-97° (from toluene).

0.0992 g sub.: 0.2314 g CO_2; 0.0994 g H_2O. 0.0162 g sub.: 0.1016 g camphor: Δt 25.5°. 0.0204 g sub.: 7.4 ml CH_4 (19°, 737 mm). Found %: C 63.59; H 11.12. $C_{14}H_{26}(OH)_4$. M 259. Calculated %: C 64.12; H 11.45. M 262. 7.2 ml CH_4.

Hydrogenation of the Liquid Having a B.p. of 99-104° (7 mm)

The experiment was carried out under the same conditions as experiment 1.

Every 12 minutes the following quantities (in ml) of hydrogen were added: 300, 168, 104, 34, 9, 3. After 70 minutes, a total of 618 ml had been added.

The hydrogenation product did not decolorize bromine water.

B.p. 96-97° (8 mm), d_{20}^{20} 0.9225, n_D^{20} 1.4486.

0.1484 g sub.: 0.3492 g CO_2; 0.160 g H_2O. 0.0412 g sub.: 18.3 g benzene: Δt 0.044°. 0.0314 g sub.: 11 ml CH_4 (18°, 743 mm). Found %: C 63.49; H 11.92. M 259.4. $C_{14}H_{26}(OH)_4$. Calculated %: C 64.14; H 11.42. M 262. 11.6 ml CH_4.

SUMMARY

For the first time, the two isomers of acetylenic erythritol — 2,4,7,9-tetramethyldecine-5-tetraol-2,4,7,9 — were synthesized and described.

The hydrogenation of the isomers in the presence of colloidal palladium was studied, and it was shown that the isomeric erythritols hydrogenated at a gradually decreasing rate, the liquid isomer hydrogenating more rapidly than the crystalline isomer.

Ethylenic and saturated erythritol, 2,4,7,9-tetramethyldecine-5-tetraol-2,4,7,9 and 2,4,7,9-tetramethyldecanetetraol-2,4,7,9 were isolated and described.

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THE DIMERIZATION OF ISOPRENE

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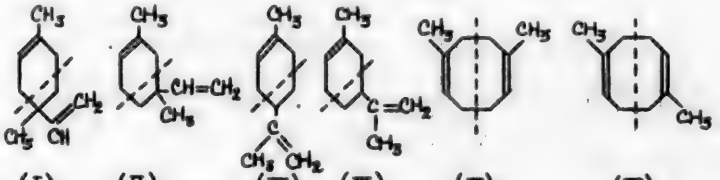
In spite of the fact that the thermal dimerization of isoprene was studied more than 75 years ago, many divergent opinions still exist concerning the structures of the dimerization products.

In the dimerization of isoprene, which proceeds according to the general type of diene condensation, the formation of four-six-membered and two eight-membered cyclic dimers (I-VI) is possible:



(I) (II) (III) (IV) (V) (VI)

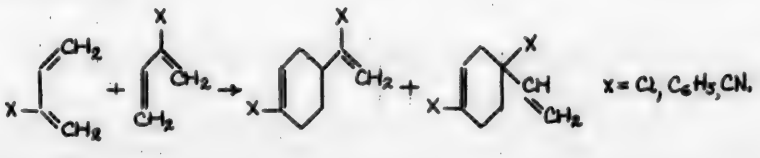
The first investigators, Bouchardat [1], Tilden [2] and Wallach [3], who studied this reaction at 280-300°, considered dipentene (III), which has a m-menthane skeleton, to be the sole product of the thermal dimerization of isoprene. In 1911 Harries [4], studying the thermal dimerization of isoprene at 150 and 300°, observed that the isoprene dimer was a heterogeneous product, and assumed that it consisted chiefly of the linear dimer with a small admixture of dipentene. In 1913 Lebedev [5], after careful distillation of the isoprene dimerization products obtained under the same conditions (at 150°), isolated two fractions and accepted them as the individual substances, dipentene (III) and 1,3-dimethyl-1-vinyl-Δ^3-cyclohexene (II), which later received the name, Lebedev's hydrocarbon. In 1924-28, Aschan [6] investigated the products obtained on storage of isoprene in an atmosphere of carbon dioxide for 10 years, and came to the opposite conclusion that, under these conditions, dipentene (III) was not the only product formed, but that the chief reaction product was a hydrocarbon, with a m-menthane skeleton, which he called diprene (IV). Ostromyslensky and Koshelev [7], as a result of the dimerization of isoprene at 80°, isolated a product which they, like Harries, accepted as the linear dimer of isoprene.

Later, Wagner-Jauregg [8], repeating the experiment of Ostromyslensky and Harries, concluded that, on dimerization of isoprene both at 86-100° and at 300°, only diprene (IV) is formed, although by dehydrogenation of the "diprene" he obtained a mixture of m- and p-cymene, with the latter predominating. He did not attribute the formation of p-cymene to the presence of the p-isomer (dipentene) in the mixture, but to the migration of the substituent from the meta- to the para-position under the influence of the catalyst ("nickel-clarite"), during the dehydrogenation process. Recently, Salomon, Boonstre, Meer and Ultee [9] polymerized isoprene in the presence of picric acid at 150°, and concluded that, under these conditions, a mixture of products, containing 80% diprene (IV), 10% Lebedev hydrocarbon (II) and 5% dipentene (III), formed.

In a study of the structural directability of the diene synthesis it was shown [10] that the condensation of asymmetrically substituted dienes with different asymmetrical dienophiles almost always yields a mixture of addition products which, for the 2-substituted dienes of the isoprene type, contain 80-90% of the para-isomer and only 10-20% of the meta-isomer.

If the cyclic dimerization of isoprene is considered as a diene condensation, we should also expect the formation chiefly of dimers having para-position substituents, i.e., dipentene (III) and 1,4-dimethyl-1-vinyl-Δ^3-cyclohexene (I).

According to literature data, the dimerization of chloroprene [11], 2-phenyl-butadiene [12] and 2-cyanobutadiene [13] proceeds in just this way:



X = Cl, C_6H_5, CN.

Nevertheless, most authors state that the chief product of the dimerization of isoprene is diprene (IV) or 1,3-dimethyl-1-vinyl-Δ^3-cyclohexene (II), i.e., the dimer having a meta-position substituent.

All of the foregoing indicates clearly how controversial and confused is the problem of the dimerization of isoprene and the structure of the dimers. As indicated above, the dimerization of isoprene has been studied by different authors at very different temperatures. The reaction products were not always carefully distilled, and their structures were not reliably demonstrated.

It was of interest to settle these problems, and to establish the structures of the dimerization products of isoprene. For this purpose, we studied the dimerization of isoprene at the temperatures 100, 150, 250 and 290°.

Carefully planned experiments, combining the use of precise distillation from an effective column, hydrogenation and dehydrogenation, and also new methods of oxidation and ozonization, enabled us to establish a realistic picture of the cyclic dimerization of isoprene, and to bring clarity to this controversial and confused problem.

TABLE 1

Effect of Temperature on the Ratio of Isoprene Dimers

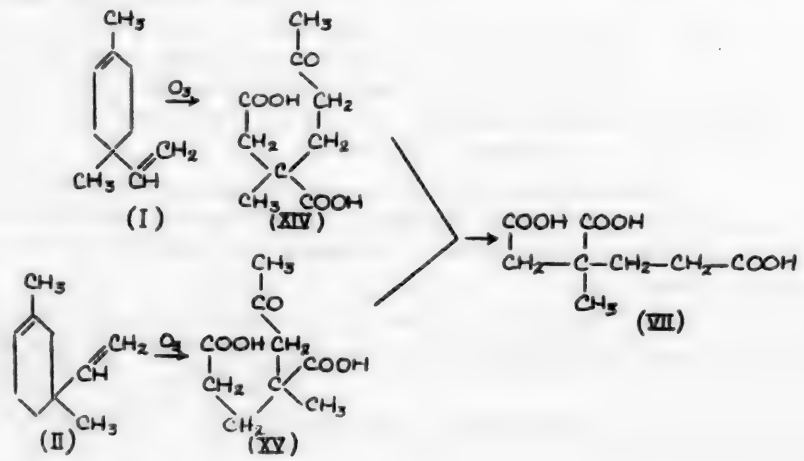
Temperature	Quantity of isoprene dimers (in %)*	
	dimers (I) and (II), b.p. 160-161°	dimers (III) and (IV), b.p. 174-175°
100°	19.2	80.8
150	22.5	77.5
250	31.3	68.7
290	42.6	57.4

Three fractions were always separated as a result of the thermal dimerization of isoprene; two of them corresponded accurately to the fractions which Lebedev [5] obtained and accepted as separate substances, but the quantitative relations between the separate fractions obtained at 100, 150, 250 and 290° were different.

Thus, as the dimerization temperature of isoprene was increased from 100 to 290°, the quantity of the low-boiling fraction, which contained a mixture of dimers (I) and (II), increased from 19.2 to 42.6%, but the quantity of the middle fraction which contained a mixture of dimers (III) and (IV), decreased from 80.8 to 57.4% (Table 1).

The low-boiling fraction (b.p. 160-161° at 760 mm), corresponding to the Lebedev hydrocarbon, is a mixture of the two heminal dimers (I) and (II), formed by the diene condensation of isoprene, and involving participation of the isopropenyl group.

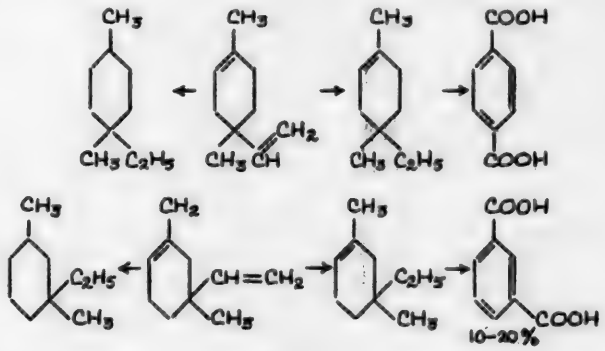
As a result of the ozonization of this fraction, a mixture of the two dicarboxylic keto acids (XIV) and (XV) was separated as an oil, which on further oxidation with peracetic acid gave 2-methyl-2-carboxyadipic acid (VII), obtained by the same methods of ozonization and oxidation as was the addition product from isoprene and methyl methacrylate. This demonstrated the presence of the methyl and vinyl groups on one carbon atom in dimers (I) and (II), since both isomers (I) and (II), after ozonization and oxidation, should yield only the acid (VII):



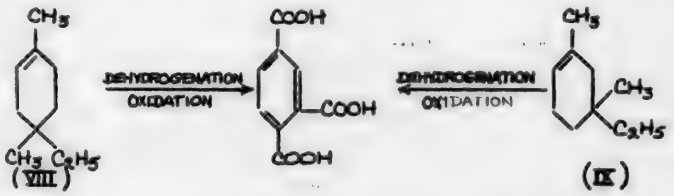
* The quantity of the eight-membered isoprene dimers (V) and (VI) increased approximately from 1.5 to 5% with the increase of temperature.

In order to demonstrate the position of the substituents in the nucleus, dimers (I) and (II), obtained as a result of the dimerization of isoprene at 100, 150, 250 and 290°, were selectively hydrogenated in the presence of platinum on carbon; in this way, we obtained a mixture of unsaturated hydrocarbons (VIII) and (IX), which contain a double bond in the ring, as shown by Pummerer and Graser [14]. Later, the unsaturated hydrocarbons (VIII) and (IX) were dehydrogenated at 340-350°, using platinum on carbon.

The dehydrogenation products were oxidized with nitric acid under pressure, and the terephthalic and isophthalic acids which separated were isolated via their barium salts and their dimethyl esters. The ratio of terephthalic acids obtained in the different experiments fluctuated within the limits 5-10:1.



Besides the terephthalic and isophthalic acids in the process described above, considerable quantities of trimellitic acid formed as a result of the migration of the heminal groups in compounds (VIII) and (IX) to the ortho-position during dehydrogenation, followed by oxidation of the hydrocarbons which formed.



Kazansky and Liberman [15] observed a similar migration for 1,1-dimethylcyclohexane.

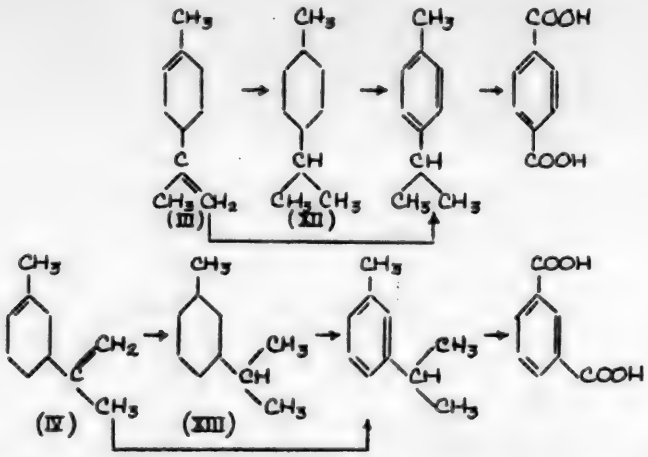
The dehydrogenation of hydrocarbons (VIII) and (IX) proceeds more smoothly than that of the isoprene dimers (I) and (II), and also more smoothly than that of the completely hydrogenated products (X) and (XI).

Thus, it was shown that the first, low-boiling fraction of the isoprene dimers which, judging from its constants, corresponds to "Lebedev's hydrocarbon", actually was a mixture of the two isomers (I) and (II), in which hydrocarbon (I), which has a para-position substituent in the cyclohexene ring, greatly predominates. It was impossible to determine accurately the quantitative ratio of isomers (I) and (II) in this fraction because of the formation of large quantities of trimellitic acid during the dehydrogenation and oxidation of hydrocarbons (VIII) and (IX). The trimellitic acid could have been formed from either of the hydrocarbons (VIII) and (IX), although hydrocarbon (IX) could give hemimellitic acid, which was practically unobserved in the dehydrogenation and oxidation products. Thus, it could be assumed that the trimellitic acid formed chiefly from hydrocarbon (VIII), corresponding to dimer (I), and consequently, that the total content of dimer (II) in the first fraction could hardly exceed 20%.

From the mixture of dimers (I) and (II) we obtained a small quantity of the crystalline nitrosochloride, which differed from the nitrosochloride of hydrocarbon (I), as described by Pummerer and Graser [14].

Investigation of the middle "dipentene" fraction (b.p. 174-175° at 760 mm) showed that it was not an individual compound, as shown by Lebedev, but that it was a mixture of dipentene (III) and diprene (IV) formed by the diene condensation of isoprene, with participation of the vinyl group.

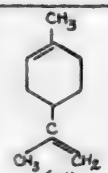
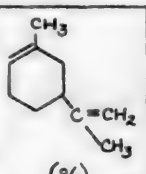
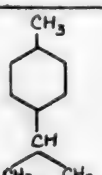
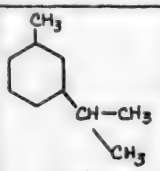
We were able to determine the ratio of isomers (III) and (IV) in this fraction rather accurately by dehydrogenation with platinum on carbon, followed by oxidation of the p- and m-cymene with dilute nitric acid, and separation of the terephthalic and isophthalic acids via their barium salts and methyl esters.



Dehydrogenation and oxidation were carried out both for a mixture of dimers (III) and (IV) and for the mixture of their corresponding menthanes and menthenes, which were obtained by exhaustive or partial hydrogenation of the dipentene fraction, but the ratio of terephthalic and isophthalic acids which resulted did not vary. In this manner, it was shown quite unexpectedly that the ratio of dipentene (II) and diprene (IV) in the dimerization products from isoprene depended very strongly on the reaction temperature.

TABLE 2

Effect of Temperature on the Ratio of Isoprene Dimers (III) and (IV). Composition of the Middle Fraction (b.p. 174-175°) Determined by Dehydrogenation and Oxidation Methods

Temperature	 (%)	 (%)	Ratio of isomers	 (%)	 (%)	Ratio of isomers
100°	20.6	79.4	1 :3.8	23.4	76.6	1 :3.2
150	28.9	71.1	1 :2.4			
250	65.2	34.8	1.8:1	62.5	34.8	1.8:1
290	75.0	25.0	3 :1			

From the adjoining Table 2 it is obvious that at 100 and 150° the chief product of the dimerization of isoprene is diprene (IV), but that at 250 and 290°, it is chiefly dipentene (III).

From the mixture of the dihydrochlorides and tetrabromides obtained from the dipentene fraction, we separated large quantities of the dihydrochloride and tetrabromide of dipentene only. A mixture of menthanes having the same constants as described by Lebedev [5] was obtained by hydrogenation of the dipentene fraction over platinum oxide.

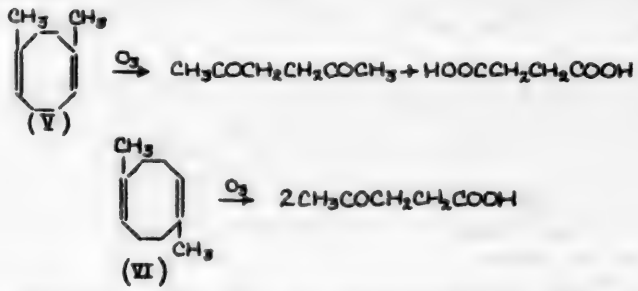
Thus, we found it interesting and astonishing that the dimerization of isoprene at reduced temperatures (100 and 150°) did not obey the usual mechanism of the structural directability of the diene synthesis, but led chiefly to the formation of diprene (IV), with a meta-position substituent. As observed above, the condensation of isoprene and other 2-substituted dienes with asymmetrical dienophiles independently of the temperature, always leads principally to addition products with para-position substituents. This interesting anomaly in the dimerization of isoprene was not observed for piperylene [16].

It is apparently impossible to account for this phenomenon on the basis of the reversibility of the diene synthesis, since on heating the dipentene fraction (obtained at 150°) for 16 hours at 250°, the ratio of dipentene (III) and diprene (IV) did not change, and also no traces of the low-boiling isoprene dimers (I) and (II) appeared.

Besides the four six-membered cyclic dimers (I), (II), (III) and (IV), in the thermal dimerization products of isoprene, we were able to demonstrate the presence of the two eight-membered cyclic dimers (V) and (VI),

the formation of which was observed under all the conditions investigated, and which increased somewhat with an increase of temperature. For the first time, the mixture of dimers (V) and (VI) was separated as a high-boiling fraction with a b.p. of 85-85.5° at 30 mm, and in a quantity of 1.5 to 5% of the total quantity of the isoprene dimers.

The structures of the isomeric dimethylcyclooctadienes (V) and (VI) were demonstrated by ozonization, by which we obtained high yields of acetonylacetone, and succinic and levulinic acids:



The presence of small quantities of formic acid in the ozonization products could be attributed to the slight contamination with dipentene (III) and diprene (IV).

EXPERIMENTAL

Isoprene was obtained by dehydration of dimethylvinylcarbinol by aluminum oxide at 300°, and had the following constants: b.p. 35°, n_D^{20} 1.4216.

In all cases, the dehydrogenation of the isoprene dimers (or products of their hydrogenation) was carried out in the vapor phase by passing the substance at a rate of 2-3 drops per minute through an 8-mm-diameter glass tube filled with catalyst, and placed vertically in an electric furnace. Platinum on carbon (15% Pt), prepared by the Linstead method [17], served as the catalyst.

Dimerization of Isoprene at 100°

1053 g of isoprene was heated at 100-105° for 36 hours in a 2-liter steel autoclave in a nitrogen atmosphere, in the presence of 10 g of hydroquinone. After the unreacted isoprene was removed (730 g), the residuals were vacuum distilled. We obtained 146 g of a mixture of isoprene dimers with a b.p. of 65.75° at 25 mm; n_D^{20} 1.4740. The residue was 60 g. The mixture of isoprene dimers (146 g) was then distilled from a 20 theoretical plate column with glass caps; the following fractions were separated: 1st, b.p. 62-62.5° (26 mm), n_D^{20} 1.4654, 23 g; 2nd, b.p. 62.5-74° (26 mm), n_D^{20} 1.4680, 10 g; 3rd, b.p. 74° (26 mm), n_D^{20} 1.4735, 84 g; residue, 7 g.

Moreover, a small quantity of the head fraction (about 1 g) with a b.p. of 100-150° at 740 mm, n_D^{20} 1.4430, was separated, but it was not investigated further.

The residuals (7 g), after distillation from the column, were separately distilled, and in this manner we obtained 5 g of a substance with a b.p. of 81-83° at 26 mm, n_D^{20} 1.4832, which was a somewhat impure mixture of the eight-membered dimers (V) and (VI).

Dimerization of Isoprene at 150°

442 g of isoprene was heated for 36 hours at 150-160° in a 1-liter steel autoclave in a nitrogen atmosphere, in the presence of 5 g of hydroquinone. The residuals were vacuum distilled after removal of the unreacted isoprene (25 g); from this we obtained 269 g (61%) of a mixture of isoprene dimers with a b.p. of 73-75° at 25 mm, n_D^{20} 1.4720. The residue was 50 g.

The mixture of isoprene dimers was then distilled using a 20 theoretical plate column with glass caps, and from this, the following fractions were separated: 1st, b.p. 55° (18 mm), n_D^{20} 1.4658, 54 g; 2nd, b.p. 55-67° (18 mm), n_D^{20} 1.4705, 10 g; 3rd, b.p. 67° (18 mm), n_D^{20} 1.4735, 185 g; residue, 9.7 g.

By distillation of the residue (9.7 g) in a Favorsky flask, we obtained 7.1 g of a mixture of the eight-membered dimers (V) and (VI) with a b.p. of 74.7-76° at 16 mm, n_D^{20} 1.4885.

Dimerization of Isoprene at 250°

530 g of isoprene was heated at 250° for 2.5 hours in a 1-liter steel ampoule in a nitrogen atmosphere, in the presence of 1% phenyl-β-naphthylamine. After removal of the unreacted isoprene, the residuals were vacuum

distilled, and we separated 464 g (87.5%) of a mixture of isoprene dimers with a b.p. of 72-78° at 28 mm, n_D^{20} 14720 This mixture of isoprene dimers was then distilled from a 20 theoretical plate column with glass caps, and we obtained the following fractions: 1st, b.p. 62-63° (26 mm), n_D^{20} 1.4655, 123 g; 2nd, b.p. 63-75° (26 mm), n_D^{20} 1.4695, 9 g; 3rd, b.p. 75-76° (27 mm), n_D^{20} 1.4735, 270 g; 4th, b.p. 76-85° (30 mm), n_D^{20} 1.4742, 11 g; 5th, b.p. 85-85.5° (30 mm), n_D^{20} 1.4842, 7 g; residue, 22 g.

Dimerization of Isoprene at 290°

A 100 ml steel ampoule containing 34 g of isoprene and 1% phenyl-β-naphthylamine, was submerged in a tin bath, and heated to 350°; the temperature of the bath was at once decreased to 285° and maintained at 285-290° for 45 minutes.

The products from the three analogous experiments were combined and vacuum distilled. In this way, 66 g of isoprene dimers (66%) with a b.p. of 64-85° at 12 mm, n_D^{22} 1.4740, was obtained. Moreover, we obtained 4 g of a substance with a b.p. of 85-139° at 12 mm, n_D^{22} 1.4900. The residue was 20 g. By redistillation of the last fraction, we obtained 2 g of the isoprene trimer, apparently, which had a b.p. of 133-135° at 12 mm, n_D^{20} 1.4940.

A mixture of the isoprene dimers (66 g) was then distilled using a column of 40 theoretical plates, from which the following fractions were obtained: 1st, b.p. 52° (16 mm), n_D^{20} 1.4645, 20 g; 2nd, b.p. 52-66° (17 mm), n_D^{20} 1.4690, 2 g; 3rd, b.p. 66° (16 mm), n_D^{20} 1.4732, 27 g; 4th, b.p. 66-78° (16 mm), n_D^{20} 1.4750, 1.2 g; 5th, b.p. 78° (16 mm), n_D^{20} 1.4850, 3.1 g.

Investigation of the low-boiling fraction of dimers (I) and (II). The low-boiling fraction was a mixture of isoprene dimers (I) and (II):

B.p. 62-63° (20 mm), 160-161° (760 mm), n_D^{20} 1.4658, d_4^{20} 0.8329; MR 45.29; calculated 45.25.

According to the data of Lebedev [5], this fraction has the following constants: b.p. 44° (9 mm), 160-161° (760 mm), $n_D^{19.7}$ 1.4658, d_4^{20} 0.8331.

Hydrogenation of a mixture of isoprene dimers (I) and (II). 24.8 g of a freshly-distilled mixture of dimers (I) and (II) (b.p. 62-63° at 26 mm), obtained from the dimerization of isoprene at 250°, was hydrogenated at 50°, in the presence of Raney nickel, and under a hydrogen pressure of 60 atm, until the absorption of hydrogen ceased. Hydrogenation proceeded energetically (about one molecule of hydrogen) at first, but toward the end it decelerated, and complete hydrogenation was attained with great difficulty. From the distillation, we obtained 20.4 g of a mixture of hydrocarbons (X) and (XI):

B.p. 163-165° (760 mm), n_D^{20} 1.4405, d_4^{20} 0.8006; MR 46.21; calculated 46.18.

By hydrogenation of this fraction over platinum oxide, Lebedev [5] obtained a hydrocarbon having the following constants:

B.p. 163-164.5° (760 mm), n_D^{20} 1.4411, d_4^{20} 0.7990.

Ozonization of a mixture of isoprene dimers (I) and (II). 8 g of a low-boiling fraction (b.p. 62-53° at 26 mm), obtained by dimerization of isoprene at 250°, was dissolved in 55 ml of 90% acetic acid, and into the solution at 0° ozonized oxygen (concentration of ozone 6%) was passed for 20 hours, until the reaction at the double bond (by decolorization of bromine) tapered off.

To the solution of the ozonide we added 36 ml of 77% peracetic acid, after which the solution was heated at 50-60° for 20 hours on a water bath, and then it was heated for 1 hour on a boiling water bath. The acetic acid was volatilized in vacuo on the water bath, and in the residue we obtained 11.1 g of a mixture of the dibasic keto acids (XIV) and (XV) as a thick, non-crystallizing oil, from which we were unable to obtain a 2,4-dinitrophenylhydrazone.

By titration we found the molecular weight of the acid to be 226. $C_9H_{14}O_5$. Calculated 202.

0.5 g of the mixture of acids (XIV) and (XV), described above, was heated for 5 hours at 100° with 2 ml of 76% peracetic acid. The acetic acid was removed in vacuo. Then 5 ml of water was added to the residue and all the volatiles were again removed in vacuo. On treatment of the residue with ether, 0.4 g of 2-methyl-2-carboxyadipic acid (VII) with a m.p. of 126-127° was separated. Mixing of the test sample with the known form obtained by ozonization of the addition product from isoprene and methyl methacrylate, produced no m.p. depression [10].

Partial Hydrogenation of the Dimers (I) and (II) with Subsequent Dehydrogenation and Oxidation

a) 10 g of a mixture of dimers (I) and (II), obtained from the dimerization of isoprene at 100° (b.p. 62-62.5° at 26 mm), was hydrogenated at 50° in a solution of 100 ml of a mixture (1:1) of methanol and ether, in the presence of 0.5 g of 15% platinum on carbon, under a hydrogen pressure of 75 atm, until approximately one molecule of hydrogen had been absorbed. The product was separated from the catalyst, diluted to twice its volume with water, extracted with ether, dried with calcium chloride and distilled. We obtained 6.5 g of a mixture of hydrocarbons (VIII) and (IX) with a b.p. of 161-166°, n_D^{20} 1.4550.

5.5 g of this mixture was dehydrogenated at 340-350° with platinum on carbon. The product was passed over the catalyst 4 times. As a result, we obtained 1.9 g of a dehydrogenation product (n_D^{20} 1.4880), which was oxidized by heating for 2 hours at 170-200° with 60 ml of 20% nitric acid, under a nitrogen pressure of 40 atm. The mixture of terephthalic and isophthalic acids was separated, washed with water, and dried (1.2 g). By concentration of the mother liquor, we obtained 1.5 g of trimellitic acid which, after recrystallization from 5% hydrochloric acid, melted at 225-227°. Mixture of a test sample with the known form of trimellitic acid showed no melting point depression.

In order to separate terephthalic and isophthalic acids (1.2 g), we heated the mixture for 20 minutes with 2.4 ml of a concentrated solution of ammonia. The precipitate was dissolved in water, the solution was concentrated to a volume of 6 ml, and mixed with a solution of 0.8 g of barium chloride in 1.4 ml of water. On the following day, the barium terephthalate which had formed was washed with water, and was decomposed by boiling for 5 hours with 2 ml of 15% hydrochloric acid.

The terephthalic acid obtained was separated, and dried in a desiccator. In this way we obtained 0.8 g of terephthalic acid with a melting point of about 320°. The filtrates, after separation of the barium terephthalate and washing with water, were combined and acidified with hydrochloric acid, yielding 0.2 g of isophthalic acid with a m.p. of about 340°.

0.8 g of the terephthalic acid described above, 20 ml of methanol and 1 ml of concentrated sulfuric acid were washed with water and dried in a desiccator. We obtained 0.85 g of dimethyl terephthalate (from ethanol), with a m.p. of 140-141°, which caused no depression of the m.p. with the known form.

0.2 g of the isophthalic acid obtained in this experiment was dissolved in 30 ml of methanol, and the solution was saturated with hydrogen chloride and allowed to stand at room temperature for 36 hours. After removal of the solvent, we obtained 0.2 g of dimethyl isophthalate (from ethanol) with a m.p. of 63-64°, and it caused no m.p. depression when mixed with the known substance. The ratio of terephthalic and isophthalic acids was 4:1.

b) 10 g of the low-boiling fraction (b.p. 55° at 18 mm) obtained from the dimerization of isoprene at 150°, was hydrogenated with platinum on carbon, as described in the preceding experiment. We obtained 7 g of a mixture of hydrocarbons (VIII) and (IX) with a b.p. of 164-166°, n_D^{18} 1.4565.

5 g of this mixture of hydrocarbons was dehydrogenated at 340-350° over platinum on carbon. We obtained 3.3 g of the dehydrogenation product (n_D^{17} 1.4905), which was oxidized by heating for 3 hours at 170-200° with 80 ml of 20% nitric acid, under a nitrogen pressure of 18 atm; in this manner, 1.6 g of terephthalic and isophthalic acids was obtained, and from the mother liquor we separated 0.9 g of trimellitic acid which, after recrystallization from 5% hydrochloric acid, melted at 225-227°, and produced no m.p. depression with the known substance.

As described above, the phthalic acids were separated as the barium salts, which were subsequently converted to the dimethyl esters. We obtained 0.9 g of dimethyl terephthalate with a m.p. of 140-141° and 0.3 g of dimethyl isophthalate with a m.p. of 63-64°. The ratio of terephthalic and isophthalic acids was 3:1.

c) 10 g of the low-boiling fraction (b.p. 62-63° at 26 mm), obtained from the dimerization of isoprene at 250°, was hydrogenated in a solution of methanol and ether in the presence of platinum on carbon, as described above. We obtained 5 g of a mixture of hydrocarbons (VIII) and (IX) (b.p. 164-166°, n_D^{18} 1.4580), which was dehydrogenated at 340-350° with platinum on carbon; in this way, we obtained 3.2 g of dehydrogenation products (n_D^{20} 1.4880), which were oxidized by heating at 170-200° with 75 ml of 20% nitric acid, under a nitrogen pressure of 40 atm. As a result, we separated 1.5 g of a mixture of terephthalic and isophthalic acids, and from the mother liquor we obtained 1.9 g of trimellitic acid which, after recrystallization from 5% hydrochloric acid, melted at 225-227°, and caused no m.p. depression with the known substance.

The phthalic acids were separated as the barium salts by the usual method, and then were converted to the dimethyl esters. We obtained 0.95 g of dimethyl terephthalate with a m.p. of 140-141°, and 0.4 g of dimethyl

isophthalate with a m.p. of 63-64°, which produced no m.p. depressions with the known substances. The ratio of terephthalic and isophthalic acids was 2.3:1.

d) 10 g of the low-boiling fraction (b.p. 52° at 16 mm), obtained by the dimerization of isoprene at 285-290° (b.p. 51.5° at 16 mm, n_D^{20} 1.4645), was hydrogenated at 50° under a hydrogen pressure of 50 atm in the presence of 1 g of 5% palladium on carbon. After the usual treatment, 9 g of a mixture of hydrocarbons (VIII) and (IX) with a b.p. of 168-170° n_D^{20} 1.4520 was obtained. 5.2 g of this mixture was dehydrogenated with Pt on carbon at 340°. We obtained 2.7 g of dehydrogenation products (n_D^{20} 1.4880), which were oxidized by heating at 200° for 3 hours with 35 ml of 20% nitric acid under a nitrogen pressure of 20 atm; in this way we obtained 2 g of a mixture of terephthalic and isophthalic acids and from the mother liquor we obtained 0.2 g of trimellitic acid which had a m.p. of 225-227°, and produced no m.p. depression when mixed with the known substance.

In order to separate the mixture of terephthalic and isophthalic acids (2 g) obtained, we dissolved it in 25 ml of a 4% soda solution. Then we added 5.6 g of barium chloride in 8 ml of water to the solution. The precipitate of barium terephthalate was separated, the filtrate was acidified with 15% hydrochloric acid, the precipitating mixture of acids (0.7 g) was separated and again dissolved in 10 ml of 5% soda solution, and 2.5 g of barium chloride in 4 ml of water was added to the solution. The barium terephthalate was filtered off, the filtrate was acidified, and in this way we separated 0.3 g of isophthalic acid, from which we obtained 0.3 g of the dimethyl ester which had a m.p. of 63-64°, and caused no m.p. depression with the known substance. The barium salts of terephthalic acid were combined and boiled with 20 ml of 15% hydrochloric acid for 30 minutes; in this way we obtained 0.9 g of terephthalic acid, from which we obtained 0.8 g of the dimethyl ester, which had a m.p. of 140-141°, and which caused no m.p. depression with the known substance. The ratio of terephthalic and isophthalic acids was 2.3:1.

Production of the nitrosochlorides from a mixture of dimers (I) and (II). At a temperature of −8°, ethyl nitrite was passed into a solution containing 17 g of a mixture of dimers (I) and (II) (obtained by dimerization of isoprene at 250°) in 20 ml of alcohol, after which 2.5 ml of water was added, and a current of hydrogen chloride was passed in at a temperature of 0 to −10°.

The reaction product was cooled to −10°, and the nitrosochloride obtained (4.5 g) was filtered off. The crystals were purified by dissolving them in chloroform and precipitating them with acetone. We obtained 1.5 g of the nitrosochloride with a m.p. of 92-92.5°.

Found %: N 6.97, 7.12. $C_{10}H_{15}ONCl$. Calculated %: N 6.95.

From hydrocarbon (I) Pummerer [14] obtained a nitrosochloride with a m.p. of 113-114°.

Investigation of the Middle Fraction of Dimers (III) and (IV).

The middle fraction of the isoprene dimers consisted of a mixture of dipentene (III) and diprene (IV).

B.p. 67° (18 mm), 74° (26 mm), 174-175° (760 mm), n_D^{20} 1.4735, d_4^{20} 0.8436; MR 45.36, calculated 45.24.

According to the data of Lebedev [5] this fraction has a b.p. of 58° (9.5 mm), 174-175° (760 mm), $n_D^{19.7}$ 1.4712, d_4^{20} 0.8454.

Dehydrogenation of a Mixture of Dimers (III) and (IV) and Oxidation of the Hydrocarbons Obtained

a) 5 g of the dipentene fraction (b.p. 74° at 26 mm, n_D^{20} 1.4735), obtained by the dimerization of isoprene at 100°, was dehydrogenated with platinum on carbon at 320-330°; we obtained 4 g of dehydrogenation products (n_D^{20} 1.4905), which were oxidized by heating at 160-200° for 3 hours with 100 ml of 20% nitric acid, under a nitrogen pressure of 40 atms. The resulting mixture of isophthalic and terephthalic acids (3.5 g) was separated by the usual method via the barium salts and dimethyl esters.

We obtained 0.6 g of dimethyl terephthalate with a m.p. of 140-141° and 2.3 g of dimethyl isophthalate with a m.p. of 63-64°. Mixtures of the test samples of these esters with the known substances showed no m.p. depressions. The ratio of terephthalic and isophthalic acids was 1:3.8.

b) 5.8 g of the dipentene fraction (b.p. 67° at 18 mm, n_D^{20} 1.4735), obtained by the dimerization of isoprene at 150°, was dehydrogenated at 320-330° with platinum on carbon; in this way we obtained 4.9 g of dehydrogenation products (n_D^{18} 1.4920), which were oxidized by heating at 160-200° for 3 hours with 110 ml of 20% nitric acid, under a nitrogen pressure of 40 atms. The resulting mixture of phthalic acids (4.2 g) was separated by the usual method via the barium salts and the dimethyl esters. We obtained 1.2 g of dimethyl terephthalate with a m.p. of 140-141° and 3 g of dimethyl isophthalate with a m.p. of 63-64°. Mixtures of test samples of these esters with the known substances produced no m.p. depressions. The ratio of terephthalic and isophthalic acids was 1:2.5.

c) 10 g of the dipentene fraction (b.p. 75-76° at 27 mm, n_D^{20} 1.4735), obtained in the dimerization of isoprene at 250°, was dehydrogenated at 325° with platinum on carbon. As a result, we obtained 6.8 g of dehydrogenation products (n_D^{20} 1.4900); 2.5 g of these products was heated for 3.5 hours at 160-200° with 60 ml of 20% nitric acid. under a nitrogen pressure of 45 atms; in this way we obtained 2.2 g of a mixture of terephthalic and isophthalic acids, which were separated as the barium salts by the usual method, followed by conversion to the dimethyl esters by means of diazomethane. We obtained 0.8 g of dimethyl terephthalate with a m.p. of 141-142° and 0.45 g of dimethyl isophthalate with a m.p. of 64-65°. Mixtures of test samples of the esters of both acids with the known substances caused no melting point depressions. The ratio of terephthalic and isophthalic acids was 1.7:1.

d) 5 g of the dipentene fraction (b.p. 66° at 16 mm, n_D^{20} 1.4732), obtained in the dimerization of isoprene at 285-290°, was dehydrogenated at 330° with 5% palladium on carbon; in this way we obtained 4.5 g of dehydrogenation products (b.p. 170-175°, n_D^{20} 1.4900), which were oxidized by heating for 3 hours at 190-200° with 100 ml of 20% nitric acid, under a nitrogen pressure of 25 atms. We obtained 3.9 g of a mixture of terephthalic and isophthalic acids, which was separated by the usual method. We obtained 2.3 g of dimethyl terephthalate with a m.p. of 140-141°, and 0.9 g of dimethyl isophthalate with a m.p. of 63-64°. Mixture of samples of these esters with the known substances gave no melting point depressions. The ratio of terephthalic and isophthalic acids was 2.5:1.

Hydrogenation of the Dipentene Fraction Followed by Dehydrogenation and Oxidation

a) 12 g of the dipentene fraction (b.p. 74° at 26 mm, n_D^{20} 1.4735), obtained as a result of the dimerization of isoprene at 100°, was hydrogenated at 50° in 100 ml of a solution of methanol and ether (1:1), in the presence of 2 g of palladium on carbon, under a hydrogen pressure of 50 atms, until the absorption of hydrogen ceased. After the usual treatment, we obtained 10 g of a mixture of hydrocarbons (XII) and (XIII) with a b.p. of 165-168°, n_D^{20} 1.4460.

5 g of this mixture was dehydrogenated at 340-350° with platinum on carbon. We obtained 4 g of dehydrogenation products (n_D^{20} 1.4900) which were oxidized by heating for 3 hours at 200-210° with 100 ml of 20% nitric acid, under a nitrogen pressure of 18 atm. We obtained 3.7 g of a mixture of phthalic acids, which were separated by the usual method. We obtained 0.9 g of dimethyl terephthalate with a m.p. of 140-141°, and 2.8 g of dimethyl isophthalate with a m.p. of 63-64°. Neither ester produced a depression of the melting point with the known substance. The ratio of terephthalic and isophthalic acids was 1:3.2.

b) 21 g of the dipentene fraction (b.p. 74-75° at 26 mm), obtained as a result of the dimerization of isoprene at 250°, was hydrogenated at 50° under a hydrogen pressure of 50 atm, over Raney nickel, until the absorption of hydrogen ceased. We obtained 16.6 g of a mixture of para- and meta-menthanes (XII) and (XIII).

B.p. 166-169° (760 mm), n_D^{20} 1.4415, d_4^{20} 0.8025; MR 46.19; calculated 46.18.

According to the data of Zelinsky and Levina [18] para-menthane had a b.p. of 168.5-169° (749 mm), n_D^{22} 1.4394, d_4^{22} 0.7985.

11 g of the mixture of menthanes (XII) and (XIII) described above was dehydrogenated at 360-370° with platinum on carbon. We obtained 9.5 g of dehydrogenation products with a b.p. of 162-173°, n_D^{20} 1.4920.

7 g of these dehydrogenation products, 49 g of chromic anhydride, 210 g of water, 210 ml of glacial acetic acid, and 70 ml of sulfuric acid were refluxed for 3 hours. The reaction product was diluted with water (200 ml). We obtained 3.8 g of a mixture of terephthalic and isophthalic acids, which were separated and converted to the methyl esters by the usual methods. We obtained 1.9 g of dimethyl terephthalate with a m.p. of 141-142° and 1.15 g of dimethyl isophthalate with a m.p. of 64-65°.

Mixed samples of both esters with the known substances did not show m.p. depressions. The ratio of terephthalic and isophthalic acids was 1.7:1.

Hydrogenation of the Dipentene Fraction in the Presence of Platinum Oxide

a) 44.8 g of a mixture of dimers (III) and (IV) (b.p. 74.5° at 26 mm, n_D^{20} 1.4735), obtained from the dimerization of isoprene at 250°, was hydrogenated in a solution of 250 ml of alcohol in the presence of 0.5 g of platinum oxide, under a hydrogen pressure of 72 atm. After removal of the alcohol, we obtained 28.0 g of a mixture of para- and meta-menthanes.

B.p. 171-172° (760 mm), n_D^{20} 1.4518, d_4^{20} 0.8168; MR 46.30; calculated 46.18.

According to the data of Lebedev [5] the hydrocarbon obtained in the hydrogenation of this fraction had a b.p. of 172-174°.

The dihydrochloride from the dipentene fraction. 42 g of the dipentene fraction (b.p. 74-75° at 26mm), obtained by the dimerization of isoprene at 250°, was stirred with 10 ml of 36% hydrochloric acid at 30-33° for 17 hours. The aqueous layer was removed, and the product was dried with calcium chloride. Upon freezing the aqueous layer, we obtained 7 g of dipentene dihydrochloride with a m.p. of 49-50°; moreover, we obtained 10 g of the liquid dichloride, with a b.p. of 110-112° (14 mm), n_D^{20} 1.4850, which we did not investigate further. Mixture of the test sample of dipentene dihydrochloride with the known substance obtained from terpineol showed no melting point depression.

We were unable to separate dipentene dihydrochloride from the dipentene fraction obtained by the dimerization of isoprene at 100°.

The tetrabromide from the dipentene fraction. On bromination of the dipentene fraction (b.p. 74° at 26 mm), obtained at 250°, in acetic acid, we obtained a 20% yield of crystalline dipentene tetrabromide, which melted at 222-224° [5] after repeated crystallization from ethyl acetate. From this fraction we obtained dipentene nitrosochloride, with a m.p. of 102-103° [14], by the usual method.

Investigation of the High-Boiling Fraction of Dimers (V) and (VI)

The high-boiling fraction consisted of a mixture of the eight-membered isoprene dimers (V) and(VI).

B.p. 83-83.5° (26 mm), n_D^{20} 1.4885, d_4^{20} 0.8745; MR 44.92; calculated 45.72.

Found %: C 88.15; H 11.85. $C_{10}H_{18}$. Calculated %: C 88.16; H 11.84.

We passed ozonized oxygen (6%) at 0°, at a rate of 5-6 liters per hour, into a solution of 2.5 g of a mixture of dimers (V) and (VI) in 50 ml of chloroform, until the reaction at the double bond (bromine in chloroform) ceased. The chloroform was removed in vacuo, and the residue was boiled with 30 ml of water until the ozonide was decomposed, then it was neutralized with soda and extracted with ether. We determined the formic acid content in the aqueous solution by the calomel method (0.12 g).

The aqueous solution was concentrated until crystallization began, then it was acidified with 5 ml of concentrated hydrochloric acid. The sodium chloride which separated was filtered off, and the solution was extracted with ether. We separated 0.5 g of succinic acid by concentrating the aqueous solution, and 0.9 g of succinic acid from the ether extract. After recrystallization, the succinic acid melted at 184-185°, and caused no m.p. depression with the known substance. Moreover, from the ether extract we obtained 0.6 g of levulinic acid with a b.p. of 155-157°, the para-nitrophenylhydrazone of which melted at 152-153°, the semicarbazone of which melted at 188°, and the mixture of which caused no m.p. depression with the known substance. After removal of the ether from the neutral products, we obtained 1.5 g of a residue from which we obtained 1.7 g of the para-nitrophenylhydrazone of acetonylacetone, which had a m.p. of 114-115°. Mixture of the test sample with the known para-nitrophenylhydrazone of acetonylacetone caused no m.p. depression.

SUMMARY

From the dimerization of isoprene in the 100-300° range we obtained all four of the theoretically possible six-membered dimers, the proportions of which varied widely with the reaction temperature.

As the dimerization temperature of isoprene was increased from 100 to 300°, the total amount of dimers (I) and (II) (b.p. 160-161°) increased from 20 to 40%, but the total quantity of dimers (III) and (IV) (b.p. 174-175°) decreased from 80 to 60%. The ratio of dimers (III) and (IV) in the middle, so-called dipentene fraction (b.p. 174-175°), changed quite sharply with the dimerization temperature. At reduced temperatures (100-150°) the chief product of the dimerization of isoprene was diprene (IV), but at elevated temperatures (250-300°) it was dipentene (III).

Thus, the dimerization of isoprene at reduced temperatures did not obey the usual mechanism of the structural directability of the diene synthesis. In all the experiments, the mixture of isoprene dimers (I) and (II) (b.p. 160-161°) contained dimer (I) with the para-substituent, as the chief product.

From the dimerization products of isoprene, for the first time, we obtained 1.5-5% yield of a mixture of both of the theoretically possible eight-membered dimers (V) and (VI), in the form of a high-boiling fraction with a b.p. of 83-83.5° at 26 mm.

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DIMERIZATION OF TRANS-PIPERYLENE

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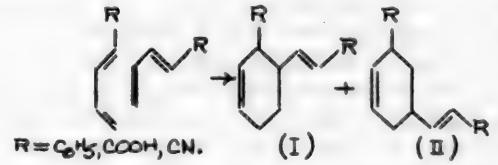
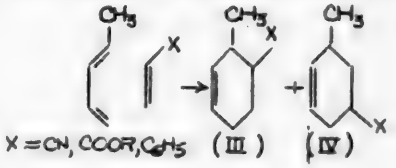
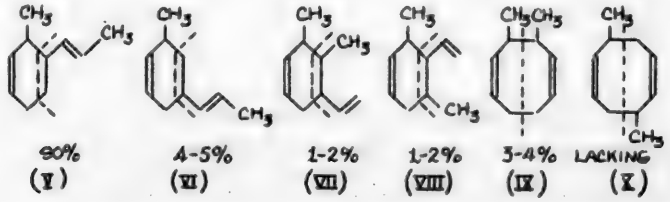
Dimerization of 1-phenylbutadiene [1], butadiene-1-carboxylic acid [2] and 1-cyanobutadiene [3] has resulted only in dimers (I) with ortho-position substituents in the ring, while efforts to obtain dimers with meta-position substituents (II) proved unsuccessful.



The dimerization of piperylene, the simplest of the 1-substituted dienes, has been little studied, and it is only most recently that Rachinsky and Zelmanovich [4] reported that at 175-180°, piperylene forms "a completely homogeneous" dimer, to which they ascribed the structure of the meta addition product (VI). As we indicated in a previous communication [5], diene condensation of piperylene with asymmetric dienophiles always results in a mixture of addition products, containing 85-95% ortho isomers (III) and only 5-15% meta isomers (IV)



Theoretically, depending upon the orientation of the molecule, dimerization of piperylene by diene condensation may produce four six-membered and two eight-membered cyclic dimers (V-X), each of which may be represented by various geometric isomers:



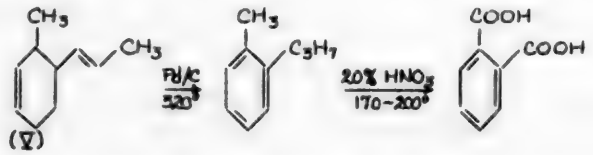
We studied the dimerization of trans-piperylene at various temperatures (140, 200, 240°), as it had been demonstrated with isoprene [6] that temperature has a very strong effect upon the nature of the dimerization product and the ratios of isomeric dimers formed (particularly dipentene and diprene).

The piperylene was heated in steel ampoules, and the dimers obtained were carefully distilled on a column of 70 theoretical plates effectiveness. As was to have been expected, the piperylene dimers consisted of a complex mixture of hydrocarbon isomers, among which we found all four of the six-membered dimers (V), (VI), (VII) and (VIII), and also one eight-membered cyclic dimer (IX). By a combination of precise distillation of large quantities of the dimers in highly-efficient columns, catalytic dehydrogenation and new methods of oxidation, we succeeded not only in definitely determining the structure of all the piperylene dimers obtained, but also in evaluating their relative quantities to a considerable degree of exactitude.

In accordance with the structurally determined direction of diene condensation of piperylene (and of other 1-substituted dienes) with asymmetric dienophiles, dimerization of piperylene results primarily in the synthesis of dimer (V), constituting about 90% of the total quantity of the dimers, and having its substituents in ortho-position

in the ring. This dimer is liberated with relative ease by distillation as the major (second) fraction, m.p. 83.5° (47 mm), n_D^{21} 1.4655.

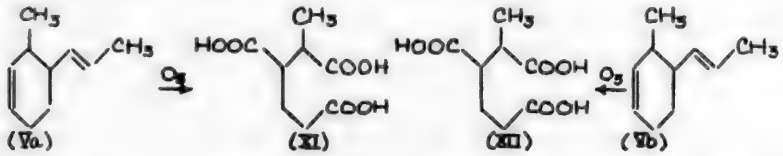
The structure of dimer (V) was determined by dehydrogenation with palladium over charcoal at 320°, and by subsequent oxidation (in phthalic acid with the aid of 20% dilute nitric acid under pressure) of the o-methylpropylbenzene formed thereby.



(V)

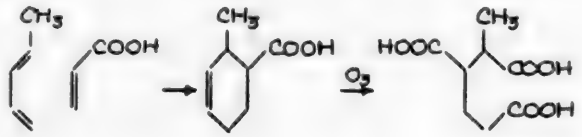
This method made it possible to oxidize the homologous aromatic acids of the most diverse aromatic compounds, including the ortho-substituted, and to obtain almost the full theoretical yield. Other oxidizing agents (permanganate, chromium trioxide, concentrated nitric acid) are of little value in the oxidation of the ortho-substituted benzene derivatives, as their use results either in low yield (not over 10-20%, moreover with formation of a complex mixture of oxidation products) or in high oxidation with cleavage of the aromatic ring. It is this that explains why Rachinsky and Zelmanovich drew an erroneous conclusion about piperylene dimer structure: they had oxidized the dimer dehydrogenation products with permanganate.

Ozonization of dimer (V) gave a high yield of a mixture of the known stereoisomeric 1-methyl-2-carboxyadipinic acids (XI) and (XII) in 7:1 ratio



(Va) (XI) (XII) (Vb)

Upon heating with concentrated hydrochloric acid at 150°, the low melting form of the acid (XII) isomerizes into the high melting (XI), which was also obtained by ozonization of the trans-piperylene addition product with acrylic acid [7]

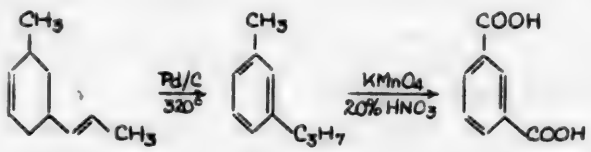


The fact that ozonization of dimer (V) yielded a mixture of stereoisomeric acids (KI) and (XII) shows that this dimer is a mixture of geometric isomers (Va) and (Vb) in a ratio of approximately 7:1.

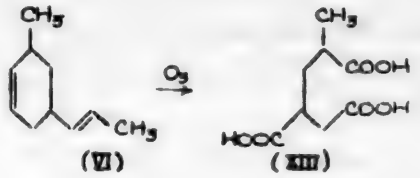
Piperylene dimerization products include only 4-5% dimer (VI), having its substituents in the meta-position within the ring.

The boiling point of this dimer is only a few degrees higher than that of dimer (V), and it, therefore, proved impossible to isolate it in pure form even upon repeated fractional distillation. It was possible, however, to concentrate dimer (VI) pretty much in the third fraction, b.p. 85.5-86° (47 mm), n_D^{22} 1.4720.

The structure of dimer (VI) was also established by its dehydrogenation and oxidation of the dehydrogenation products in isophthalic acid, both with permanganate and with dilute nitric acid under pressure

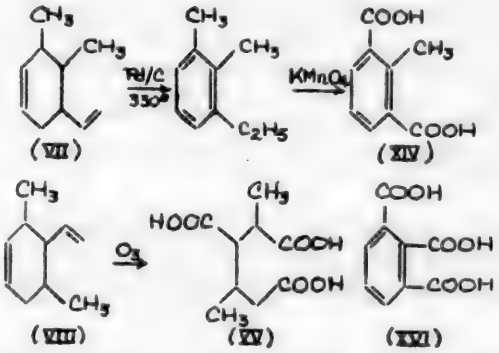


Ozonization of the third fraction (b.p. 85.5-86° at 47 mm) containing dimer (VI) liberated 1-methyl-3-carboxyadipinic acid (XIII), which has been described in the literature [8], but efforts to isolate it completely proved unsuccessful because of the small quantity synthesized



(VI) (XIII)

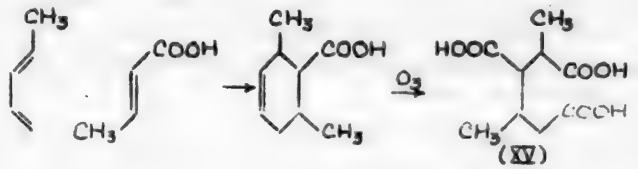
Dimers (VII) and (VIII) were formed upon thermal dimerization of piperylene only to a quantity of 1-2% of the total, but it proved possible to concentrate them in the first, low-boiling, fraction, b.p. 77-80° (47 mm), n_D^{22} 1.4625. These dimers also could not be isolated in pure form, but their presence was determined beyond question by dehydrogenation and oxidation of the first fraction, and also by the ozonization thereof; this resulted in the liberation of 2-methyl-isophthalic acid (XIV), which has been described in the literature [9], and which corresponds to dimer (VII) and 1,3-dimethyl-2-carboxyadipinic acid (XV), corresponding to dimer (VIII):



(VII) (XIV)

(VIII) (XV) (XVI)

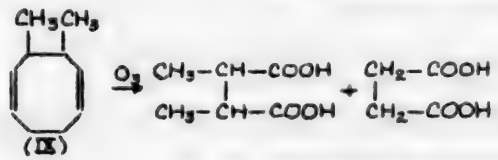
We also obtained tricarboxylic acid (XV) by ozonization of the transpiperylene addition product with crotonic acid [5]:



(XV)

Oxidation of dehydrogenation products of the first fraction with dilute nitric acid under pressure, yielded hemimellitic acid (XVI), which also substantiates the presence of dimers (VII) and (VIII).

The eight-membered cyclic dimer, piperylene (IX) was obtained as the fourth, high boiling, fraction, b.p. 93-94° (47 mm), n_D^{20} 1.4825. The structure of this dimer was revealed by ozonization, which gave a high yield of succinic and dimethylsuccinic acids. The latter was also obtained in its meso-form, m.p. 197-198°, which testifies to the cis-position of the methyl groups in dimer (IX):



(IX)

Racemic dimethylsuccinic acid, corresponding to dimer (IX) with methyl groups in trans-position, and methylsuccinic acid, corresponding to dimer (X) do not appear upon ozonization, and, consequently, these compounds are lacking among the piperylene dimerization products.

Unlike isoprene, the ratios of the piperylene dimers do not depend very much upon dimerization temperature in the 140-240° temperature interval.

EXPERIMENTAL

Ordinary piperylene (b.p. 41-42.5°, n_D^{20} 1.4320) was obtained by distillation of the piperylene fraction resulting from synthesis of divinyl by the S. V. Lebedev method. Trans-piperylene was obtained by isomerization of standard piperylene by heating it with iodine [10], and showed the following constants: b.p. 41.5°, n_D^{20} 1.4308 (trans-form content: 92%).

Catalytic dehydrogenation of the piperylene dimers was effected in a glass tube, 8-9 mm diameter, heated by an electric heater in vertical position. Substance was placed in the top end at a rate of 4-5 drops per minute. The catalyst was palladium on charcoal (5-10% palladium) prepared by the Linstead method [11]. The layer of catalyst in the tube was 25-30 cm high.

Determination of Piperylene Trans-Form Content. Synthesis of Piperylene Adduct with Maleic Anhydride

160 g twice-sublimed maleic anhydride, 0.1 g picric acid were taken, to which 136 g standard piperylene (b.p. 41-42.5°, n_D^{20} 1.4320) was added gradually with ice-water cooling. After 10 hours, 500 ml toluene was added to the reaction mixture, which was then heated on a water bath at 50° for six hours. Upon distillation on a column at atmospheric pressure, 40 g cis-piperylene was obtained, b.p. 43°, n_D^{20} 1.4350. After the piperylene had been driven off, the toluene was vacuum distilled, and the residue recrystallized from a 9:1 petroleum ether and benzene mixture; this gave 210 g adduct, m.p. 60-61°, corresponding to 84 g trans-piperylene.

Thus, standard piperylene contains about 30% of the cis- and 70% of the trans-isomer.

Isomerization of Industrial Piperylene and Determination of Content of Trans-Form in the Isomerized Product

10 g iodine was added to 136 g standard piperylene. The iodine was dissolved in the piperylene upon heating. The solution was permitted to stand overnight, and was boiled for an hour the next day, the product being distilled on a column of 20 theoretical plates at atmospheric pressure; this yielded 122 g isomerized piperylene, b.p. 41.5°, n_D^{20} 1.4308.

40 g isomerized piperylene and 0.1 g picric acid dissolved in 200 ml benzene were mixed with 56 g twice-sublimed maleic anhydride; ice-water cooling. The solution was permitted to stand overnight at room temperature and was then boiled 6 hours, with a reflux condenser. The reaction product, when distilled in a column, yielded 1.5 g cis-piperylene, b.p. 43°, n_D^{20} 1.4350. All the benzene was then vacuum distilled, and the residue recrystallized from a mixture of benzene and petroleum ether. This gave 89 g adduct, m.p. 60-61°. The trans-piperylene content in the isomerized product was 92%.

Piperylene Dimerization

1) 90 g trans-piperylene (b.p. 41.5°, n_D^{20} 1.4308) was heated in a steel ampoule in presence of 0.1 g hydroquinone at 140° for 10 hours. Distillation gave 52.5 g unreacted piperylene (b.p. 41.5-42°) and 15 g dimers, b.p. 60-62 (20 mm), n_D^{20} 1.4690.

2) 40 g trans-piperylene was heated in a steel ampoule at 190° for 2 hours. Vacuum distillation gave 28 g (70%) dimer mixture, b.p. 60-75° (18 mm), n_D^{20} 1.4680.

3) 102 g trans-piperylene was heated in a steel ampoule at 240° for 2 hours. Vacuum distillation gave 82 g (80%) piperylene dimers, b.p. 52.5° (15 mm), n_D^{20} 1.4692.

4) 14 g standard piperylene was heated in a steel ampoule at 190° for 4 hours. Vacuum distillation gave 3 g (22%) dimer mixture, b.p. 60-72° (18 mm), n_D^{20} 1.4685.

5) 21.5 g standard piperylene and a crystal of iodine were heated in a steel ampoule at 190° for 4 hours. Vacuum distillation gave 10 g dimers, b.p. 60-75° (18 mm), n_D^{20} 1.4680.

360 g mixture of trans-piperylene dimers, obtained at 240°, were vacuum distilled at 47 mm in a column of 70 theoretical plates. This gave the following major fractions: 1st, b.p. 77-80°, n_D^{22} 1.4625, 32 g; 2nd, b.p. 83.5°, n_D^{21} 1.4655, 230 g; 3rd, b.p. 85-86°, n_D^{22} 1.4720, 32 g; 4th, b.p. 93-94°, n_D^{20} 1.4825, 19 g.

The first fraction was an approximately 5:1:1 mixture of piperylenes (V), (VII), (VIII). Repeated distillation of this fraction failed to produce (VII) and (VIII) in pure form.

The second fraction (d_4^{20} 0.8360) consisted of piperylene dimer (V) with a small admixture (about 5%) of meta-isomer (VI).

Found %: C 87.89, 87.99; H 12.10, 11.93. $C_{10}H_{16}$. Calculated %: C 88.16; H 11.75.

The third fraction consisted of an approximate 4:1 mixture of piperylene dimers (V) and (VI).

Redistillation of this fraction failed to isolate meta-isomer (VI) in pure form.

Found %: C 88.10, 88.14; H 12.03, 11.99. $C_{10}H_{16}$. Calculated %: C 88.16; H 11.75.

The fourth fraction consisted chiefly of the eight-membered cyclic piperylene dimer (IX). Upon redistillation on a column this dimer was readily obtained in pure form, b.p. 81.5° (33 mm), n_D^{20} 1.4860, d_4^{20} 0.8749.

Found %: C 87.95, 88.10; H 12.10, 11.94. $C_{10}H_{16}$. Calculated %: C 88.16; H 11.75.

Dehydrogenation and oxidation of Fraction I. 5.2 g of the first fraction (b.p. 77-80° at 47 mm) was dehydrogenated over 10% palladium on charcoal at 330-335° for five hours. This yielded 3.4 g dehydrogenation products, b.p. 165-175°, n_D^{20} 1.4910.

a) 1.6 g dehydrogenation products were heated with 300 ml 5% permanganate solution at 80° for 6 hours. The permanganate excess was decolorized with methanol, the precipitated manganese dioxide filtered off, and the filtrate evaporated to $\frac{1}{6}$ its initial volume. The hot solution was acidified with 12 ml concentrated sulfuric acid, and, after cooling, was extracted 4 times with ethyl acetate (200 ml all told). The solvent was driven off, and the residue recrystallized from hot water. This yielded 0.2 g 2-methyl-isophthalic acid (XIV), m.p. 227-228°, which gave no depression with a known sample.

b) 1.6 g dehydrogenation products were oxidized by 60 ml 30% nitric acid under 40 atms nitrogen pressure at 170-200° for 3 hours. The solution of oxidation products was evaporated to dryness, and the resultant mixture of acids (1.4 g) dissolved in 25 ml hot 10% hydrochloric acid, a solution of 0.5 g calcium chloride in 25 ml 10% hydrochloric acid being added to the hot solution. Upon cooling of the solution, 0.5 g of the potassium salt of hemimellitic acid came down, which was filtered off and dissolved in 3 ml concentrated ammonia solution. The solution was boiled on a water bath until the ammonia odor disappeared, whereupon 3 ml water was added, and a solution of 0.25 g barium chloride in 3 ml water was poured into the hot solution. The precipitated barium salt was separated off, washed with 2 ml of water. To the precipitated Ba salt was added 20 ml of 5% sulfuric acid, and the mixture was boiled for 1 hour. The resulting barium sulfate was filtered out of the hot solution and washed with 10 ml of hot water. The filtrate and the wash waters were merged and evaporated to dryness. After recrystallization from 10% hydrochloric acid, 0.3 g hemimellitic acid (XVI) was obtained, m.p. 196-197°, which gave no depression combined with a known sample.

After the hemimellitic acid potassium salt was removed, the filtrate was evaporated to dryness, and the residue extracted with absolute alcohol. The alcohol was driven off, and the residue recrystallized from hot water. This yielded 0.9 g o-phthalic acid, m.p. 190-191°, corresponding to dimer (V), and this gave no depression with a known sample of phthalic acid.

Ozonization of the first fraction. 3 ml of the first fraction, dissolved in 50 ml 90% acetic acid, was ozonized at 0° for 6 hours (6% ozone concentration). 12 ml 70% peracetic acid was added to the ozonide solution, and the mixture heated to 60-65° for 12 hours. The acetic acid and the peracetic acid excess were driven off in vacuum. This gave an oil, which crystallized after lengthy washing in 20% hydrochloric acid. After recrystallization from 5% hydrochloric acid, this gave 2 g acid (XI), m.p. 175-176°, which gave no depression with a known sample. In addition, 0.1 g acid (XV) was obtained, m.p. 178-180°, giving no depression with a sample of 1,3-dimethyl-2-carboxyadipinic acid (m.p. 182-183°) (obtained by ozonization of the trans-piperylene adduct with trans-crotonic acid).

A mixed sample of these substances melted at 178-182°. Mixture of acids (XI) and (XV) gave a depression of melting point, and melted at 143-155°.

Dehydrogenation and oxidation of the second fraction. 10 g second fraction (b.p. 83.5° at 47 mm) was dehydrogenated over 5% palladium on charcoal at 320° for 10 hours. This gave 7.2 g dehydrogenation products, b.p. 175-180°, n_D^{20} 1.4890.

a) 2.8 g dehydrogenation products were oxidized by means of 50 ml 20% nitric acid at 25 nitrogen atm pressure and 170-200° in 4 hours.

After condensation in vacuum of the oxidation products solution and crystallization of the residue (2.6 g) from hot water, 2.3 g o-phthalic acid, m.p. 190-191° was obtained, which gave no depression of melting point with a known sample. The anilide of this acid melted at 208° and also gave no depression with a known sample

of o-phthalic acid anilide. Further, this experiment also yielded 0.1 g isophthalic acid, m.p. 330-335°, the dimethyl ester of which melted at 64-65° and gave no depression with a known sample.

b) 3 g dehydrogenation products were boiled, with a reflux condenser, in 25 ml 35% nitric acid. The resultant oil was extracted with a 10% sodium hydroxide solution, the alkaline extract was acidified with 20% hydrochloric acid, and the solution extracted with ether. After the ether was driven off and the residue redistilled, this yielded 0.05 g o-phthalic acid, m.p. 190-192°, which gave no depression with a known sample.

c) 1 g dehydrogenation products were acidified by a solution of 10 g permanganate and 0.5 g potassium hydroxide in 300 ml water at 90° for 8 hours. The permanganate excess was decolorized with methanol, the precipitated manganese dioxide filtered off, and the filtrate condensed to half its volume. The solution was acidified with concentrated hydrochloric acid and then extracted with ether. The ether was driven off, and the residue recrystallized from water. This gave 0.05 g isophthalic acid, m.p. 320-330°, the dimethyl ester of which melted at 64-65° and gave no depression with a known sample.

Ozonization of the second fraction. 4 g second fraction dissolved in 50 ml 95% acetic acid was ozonized at 0° for 8 hours (6% ozone concentration). A mixture of 10 ml 30% hydrogen peroxide, 30 ml acetic acid and 0.5 ml concentrated sulfuric acid was added to the ozonide solution. The solution was heated at 55-75° for 10 hours, whereupon another 10 ml 30% hydrogen peroxide was added, and heating continued another 5 hours. After addition of 1.5 g sodium acetate the solution was vacuum condensed to dryness. The dry residue was extracted with absolute alcohol, and 2.7 g acid mixture was obtained after the alcohol was driven off; crystallization of the mixture from 10% hydrochloric acid gave 2 g of the high boiling form of 1-methyl-2-carboxyadipinic acid (XI), m.p. 176-177°, which gave no depression with a known sample obtained from the ozonization of the trans-piperylene adduct with acrylic acid. Also obtained was 0.3 g of the low boiling form of 1-methyl-2-carboxyadipinic acid (XII), m.p. 140-141°, also giving no depression with a known sample [8].

Isomerization of acid (XII). 0.2 g acid (XII), m.p. 140-141° was heated in a sealed tube with 10 ml concentrated hydrochloric acid at 150° for 5 hours. This yielded 0.1 g acid (XI), m.p. 175-176°, which gave no depression with a known sample.

Hydrogenation of Fraction II. 20 g Fraction II was hydrogenated in presence of platinum oxide. 6.3 liters hydrogen was absorbed (theoretically 6.5 liters). The catalyst was filtered off, and the residue distilled. This yielded 17 g of a mixture of geometric isomers of 1-methyl-2-propylcyclohexane, b.p. 173.5-175°, n_D^{20} 1.4412.

Dehydrogenation of Fraction III and oxidation of dehydrogenation products. 6.0 g Fraction III (b.p. 85-86° at 47 mm was dehydrogenated in vapor over 10% palladium on coal at 325-330° in the course of 6 hours. This gave 4.3 g dehydration products, b.p. 160-175°, n_D^{20} 1.4920.

a) 1.6 g dehydrogenation products were boiled with a solution of 15 g permanganate and 1.5 g potassium hydroxide in 300 ml water, for 15 hours. The permanganate excess was decolorized with methanol, and the manganese dioxide filtered off from the hot solution. The filtrate was condensed to $\frac{1}{5}$ its initial volume, acidified with 6 ml concentrated sulfuric acid and thrice extracted with ethyl acetate. After the ethyl acetate was driven off, this gave 0.3 g isophthalic acid, m.p. 330-335°, the dimethyl ester of which melted at 64-65°, and gave no depression with a known sample.

b) 2.7 g dehydrogenation products were heated with 60 ml 20% nitric acid at 180-200° under 30 atm nitrogen pressure for 4 hours. The solution was evaporated to dryness, and the residue crystallized from hot water. This yielded 2.2 g o-phthalic acid, m.p. 190-191°, giving no depression with a known sample. The anilide of the acid melted at 208° and also gave no depression with phthalic acid anilide. Also obtained was 0.4 g isophthalic acid m.p. 328-335°, the dimethyl ester of which melted at 64-65° and gave no depression with a known sample.

Ozonization of Fraction III. 1.6 g of the third fraction was ozonized in a solution of 28 ml 90% acetic acid at 0°, for 4 hours. 10 ml 30% hydrogen peroxide, 30 ml acetic acid and 0.5 ml concentrated sulfuric acid were added to the ozonide solution, and the mixture was heated for 12 hours at 65-75°. After the addition of 1 g sodium acetate, it was evaporated to dryness, the residue extracted with dry ethanol, and after vacuum distillation of the ethanol it was recrystallized from 10% hydrochloric acid. This yielded 0.5 g of the high melting form of 1-methyl-2-carboxyadipinic acid (XI), m.p. 176-177°, which gave no depression with a known sample. Also obtained was 0.1 g acid, m.p. 148-150° (with decomposition) apparently consisting of 1-methyl-3-carboxyadipinic acid (XIII), which it proved impossible to purify because of the small quantity available (m.p. 158° according to the literature). This acid gave a 30° melting point depression with the acids described above (XI) and (XII). 0.1 g acid (XIII) (m.p. 148-150°) was heated in an ampoule with 8 ml concentrated hydrochloric acid at 150° for 2 hours. This gave 0.04 g acid, m.p. 130-134°, which was not subjected to further study.

Ozonization of the fourth fraction. 3.2 g fourth fraction (b.p. 81.5° at 33 mm) was ozonized in a 50 ml 90% acetic acid solution at 0° for 6 hours (ozone concentration 6%). 12 ml 70% peracetic acid was added to the ozonide solution, and the mixture was heated at 65-75° for 10 hours. The solution was vacuum condensed until dry, and the residual (3.14 g) acid mixture was crystallized from hot water. This yielded 1.4 g meso-dimethylsuccinic acid, m.p. 197-198° (rapid melting, accompanied by decomposition), which gave no depression with a known sample. Methylsuccinic acid, and racemic dimethylsuccinic acid did not appear in the aqueous mother liquors.

Dehydrogenation and Oxidation of a Mixture of Piperylene Dimers Obtained at 240°

6 g dimer mixture (b.p. 52-59° at 15 mm, n_D^{20} 1.4692) was passed over 5% palladium on charcoal at 310° for 4 hours. Yield 4.5 g dehydrogenation products, b.p. 160-170°, n_D^{20} 1.4925. 1.5 g of these dehydrogenation products was oxidized with 25 ml 20% nitric acid at 200° for 3 hours under 20 atm nitrogen pressure.

After condensation of the solution and recrystallization of the residue from hot water, this yielded 1.2 g o-phthalic acid, m.p. 190-191°, which gave no depression with a known sample, and 0.10 g isophthalic acid, m.p 328-333°, the dimethyl ester of which melted at 64-65° and also gave no depression when mixed with a known sample.

Dehydrogenation and Oxidation of Piperylene Dimer Mixture Obtained at 140°.

5 g dimer mixture (b.p. 60-62° at 20 mm) was passed over 5% palladium on charcoal at 320° in 3 hours. Yield, 2 g dehydrogenation products (b.p. 160-175°, n_D^{20} 1.4900), which were oxidized by means of 48 ml 20% nitric acid under 20 atm nitrogen pressure for 3 hours at 180-200°. After evaporation of the solution and recrystallization of the residue from hot water, 1.3 g o-phthalic acid, m.p. 190-191° was obtained, which gave no depression with a known sample. In addition, 0.06 g isophthalic acid, m.p. 333-335° was obtained, the dimethyl ester of which melted at 64-65° and also gave no depression with a known sample.

SUMMARY

The thermal dimerization of trans-piperylene at 140, 200 and 240° was studied; it was shown that this resulted in the formation of a complex mixture of dimers, containing 90% of the ortho-isomer (V), 4-5% of the meta-isomers (VI), 1-2% of the adjacent isomers (VII), (VIII) and 3-4% of the 8-membered cyclic dimer (IX).

The six-membered dimer (V) takes the form of a mixture of two geometric isomers (Va) and (Vb), in which the first predominates overwhelmingly (cis-position of the methyl and propenyl groups). The 8-membered dimer (IX) is synthesized only in one geometric form, with the methyl groups in cis-position.

The other possible 8-membered structural isomer (X) does not come into being at all.

As distinct from the case of isoprene, the temperature at which dimerization is performed has no serious effect upon the ratio of the six-membered cyclic dimers of trans-piperylene.

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* See Consultants Bureau Translation, page 75.
** See Consultants Bureau Translation, page 291.
*** See Consultants Bureau Translation, page 73.

INVESTIGATIONS IN THE FIELD OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XVII. CYCLOOCTYNE

N. A. Domnin and T. D. Malysheva

In 1938 one of us [1] in studying the action of metallic sodium on 1-chloro-2-bromo-1-cyclooctene in anhydrous ether in sealed tubes obtained a hydrocarbon, which, from the results of studying its composition, its physical and chemical properties and a proof of its structure, corresponded to cyclooctyne. At the time we had to limit ourselves to only chemical methods for proving the structure of the hydrocarbon (oxidation and ozonolysis), which, as was shown later [2], proved to be insufficiently convincing and inadequate.

In 1947 a study of the obtained hydrocarbon was resumed, and together with T. D. Malysheva, we obtained the Raman spectrum. The frequencies of the lines found in this spectrum are given in the table.

TABLE

Frequency	Intensity	Frequency	Intensity
150	(2)	1076	(2)
198	(2)	1238	(4)
243	(4)	1270	(7)
365	(3)	1332	(5)
475	(1)	1445	(10)
586	(1)	1614	(1)
705	(5)	1634	(4)
747	(2)	1653	(5)
768	(4)	2112	(4)
857	(1)	2932	(10)
908	(3)	2971	(10)
966	(3)	3050	(10)
1000	(1)	3133	(10)
1038	(1)		

The presence in the spectrum of line 2112 cm^{-1} definitely indicates the presence of a triple bond in the studied hydrocarbon. But the presence of lines 1614 (1), 1634 (4) and 1653 (5), characteristic for the double bond, apparently, is evidence that the investigated hydrocarbon is not homogeneous, but instead that it is a mixture, consisting at least of a hydrocarbon with a triple bond and a hydrocarbon with a double bond, and possibly, of even a greater number of hydrocarbons.

After these studies about 1.5 g of the hydrocarbon (b.p. 72-76° at 100 mm, n_{α}^{15} 1.463, d_4^{15} 0.844) was oxidized with potassium permanganate by L. I. Yarmolitska; on doing this, suberic acid was obtained in excellent yield.

These results permit making the assumption that the hydrocarbon mixture, obtained in the action of metallic sodium on 1-chloro-2-bromo-1-cyclooctene, consists of cyclooctyne and cyclooctene, the latter being capable of existing in the cis- and trans-forms. It is possible that other substances are also present in the mixture.

In 1953 Blomquist and Liang Huang Liu [2] published a paper in which they also synthesized cyclooctyne. After chromatographic purification, they isolated cyclooctyne in the pure form and proved its structure by way of infra-red spectral analysis (IR spectrum 4.53 mμ), ozonolysis, hydrogenation, and hydration.

Consequently, as it follows from our investigations and the more detailed studies of Blomquist and Liang Huang Liu, the ability for cyclooctyne to exist was demonstrated.

At the time we failed to publish this additional and new data on cyclooctyne for the reason that we considered it necessary to study the problem further.

We wish to express our deep gratitude to M. V. Volkenshtein for making the spectroscopic studies possible.

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Leningrad State University

CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

XV. QUINOLINE DERIVATIVES WITH THE SIDE CHAIN CYCLIC SUBSTITUENTS CONNECTED TO THE NUCLEUS AT THE 4-POSITION THROUGH THE NH GROUP

V. I. Stavrovskaya

The replacement of the aliphatic diamine in acridine antimalarial compounds by benzyldiethylamines led to substances, the activity of which approaches the activity of atebrin, exceeding it by several times in isolated cases [1]. The biological data on the synthesized acridine compounds, and also the conclusions of Magidson and Rubtsov [2], showing that in the transfer of the side chain from the 8-position of 6-methoxy-8-aminoquinoline to the 4-position there is observed an increase in the schizotropic and a loss in gamotropic properties, served as a base for the synthesis of quinoline derivatives with the side chain cyclic substituents connected to the nucleus at the 4-position through the NH group.

For the synthesis of these compounds only those aromatic amines were used that, on being introduced into the acridine nucleus, gave substances possessing clearly defined antimalarial activity. The compounds synthesized by us are given in the table. The structure of 7-chloro-4-(3'-diethylaminomethylphenyl)-aminoquinoline (I) was further varied by the introduction of hydroxy and methoxy groups (II,* III).

As in the case of the acridine nucleus, we tried to increase the antimalarial activity by the introduction of a second diethylaminomethylene group in the ortho-position to the hydroxyl and the meta-position to the NH group (V). It should be mentioned that compounds of this type are not disclosed in the literature. In addition, we synthesized two compounds with side chain cyclic substituents that had been obtained by us in the synthesis of 2-hydroxy-5-nitrobenzyldiethylamine and in the elucidation of its structure (IV, VI).

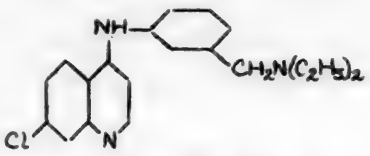
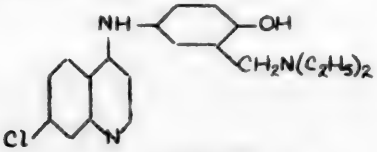
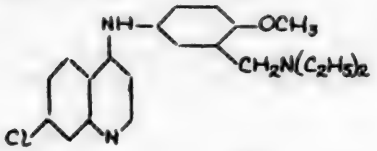
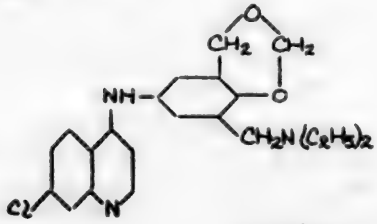
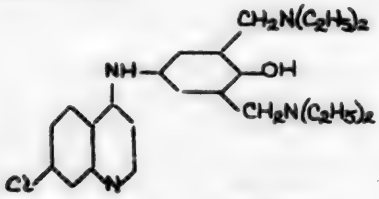
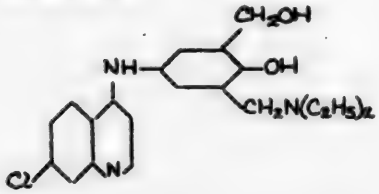
The synthesis of quinoline compounds with side chain cyclic substituents was accomplished by three methods: 1) by heating 4,7-dichloroquinoline with an aromatic amine at 160-180° (I, III); 2) by heating 4,7-dichloroquinoline and the proper amine in weakly acid medium for 2 hours (II, IV, V, VI); 3) via the Mannich reaction from 7-chloro-4-(4'-hydroxyphenyl)-aminoquinoline, formaldehyde and the proper aromatic amine [5]. The most general and convenient method is the second: heating of 4,7-dichloroquinoline with the aromatic amine in weakly acid medium. The compounds are obtained pure and in excellent yield. On cooling the reaction mass, some of the compounds crystallize out as the hydrochlorides. However, for those compounds in which a hydroxy group is present in the side chain cyclic substituent, the most convenient is the third method — the Mannich reaction. In this case there is no need to separately synthesize the complex aromatic amines; 7-chloro-4-(4'-hydroxyphenyl)aminoquinoline is readily obtained in quantitative yield. If molal amounts of all of the components are taken in the Mannich reaction, then the compound formed is one in which one hydrogen atom has been replaced by the diethylaminomethylene group. Accompanying this compound in very small amounts is the compound in which both hydrogen atoms, found in the ortho-position to the hydroxyl, have been replaced by diethylaminomethylene groups (V). If for the reaction, a double amount of formaldehyde and a considerable excess (5-8 times) of diethylamine are taken, then a mixture of substances is obtained, consisting for the most part of the second compound and only a very small amount of the first.

The mixture of mono- and dibasic Mannich bases obtained in the Mannich reaction was separated by the method developed by us, based on the different solubility of these compounds in ether. While the dibasic compound is readily soluble in ether, the monobasic compound is practically insoluble in ether. The reason for this is apparently inner salt formation between the acidic hydroxyl group and the basic $N(C_2H_5)_2$ group. The dibasic compound also suffers a similar reaction, but the presence of a second diethylaminomethylene group communicates a more basic character to the compound. The observed difference in the solubilities of the mono- and dibasic Mannich compounds proved to be extremely important, inasmuch as it permitted us to separate with comparative ease the highly active dibasic compounds from the less active monobasic Mannich compounds.

The Mannich bases of the synthesized quinoline compounds with side chain cyclic substituents are light yellow

* II was synthesized abroad earlier (Samoquin [3]); however, we prepared the compound before the appearance of the papers on its methods of synthesis [4].

TABLE

Preparation No.	Formula	Melting point: base	Melting point: hydrochloride
I		158°	126-128°
II		207	183-184
III		201-202	198-199 (decomp.)
IV		177	Oxalate 198 (decomp.)
V		160-162	Oxalate 154-155 (decomp.)
VI		–	Picrate 162-164 (decomp.)

solids. They are soluble in alcohol, benzene, acetone, and dilute acids; insoluble in water and dilute alkalis. As a rule, the hydrochlorides are yellow and readily soluble in water.

When the synthesized compounds were tested on P. relictum infection in siskins and linnets, all of them were shown to possess schizotropic activity. In the order of their antimalarial activity the synthesized compounds can be arranged as follows: V is 3-4 times as active as chloroquine and 10 times as active as atebrin; its toxicity is below that of chloroquine and close to that of atebrin; II is approximately equal to chloroquine in activity and is 3 times as active as atebrin; its toxicity is below that of chloroquine, close to the toxicity of atebrin; III and VI are close to atebrin in activity, while their toxicity is below that of the latter; in the case of I and IV, both the activity and toxicity are below that of atebrin.

As a result, in quinoline compounds the same relationship exists between antimalarial activity and chemical structure as was found to hold true in the case of the acridines, namely: the replacement of the side aliphatic "chain" by m-aminobenzyldiethylamine and its derivatives leads to highly active schizotropic substances; the t toxicity of all of the compounds is below the toxicity of chloroquine. The antimalarial activity is clearly manifested when m-aminobenzyldiethylamine is present as a side chain substituent. Methoxy and hydroxy groups,

introduced in the para-position to the NH group, increase this activity. In contrast to acridine compounds, the introduction of a second diethylamino group in the ortho-position to the hydroxyl sharply augments the antimalarial activity when compared with the compound in which only one diethylamino group is present.

We wish to thank Prof. Sh. D. Moshkovsky and S. A. Syrkina for making the biological studies.

EXPERIMENTAL

7-Chloro-4-(3'-diethylaminomethylphenyl)aminoquinoline (I)

A mixture of 4,7-dichloroquinoline (2 g) and m-aminobenzyldiethylamine (2 g) was heated in an oil bath at 160-180° for 18 hours. The obtained solid product was dissolved in 50% acetic acid, filtered, and made alkaline with a 10% sodium hydroxide solution. The deposited viscous dark brown base was extracted with ether. The ether solution was washed with water and then dried over potash. After distilling off the ether there remained 3.6 g of dark red viscous liquid, which gradually began to crystallize. The compound was purified by recrystallization from acetone and from benzene-petroleum ether mixture. Needles, m.p. 158°.* The base is a light yellow compound; extremely soluble in alcohol, acetone and benzene, readily soluble in ether, poorly soluble in petroleum ether, insoluble in water; easily soluble in dilute acids.

4.890 mg sub.: 0.539 ml N_2 (19°, 738 mm). 4.543 mg sub.: 0.510 ml N_2 (19°, 729 mm). Found %: N 12.51, 12.59. $C_{20}H_{22}N_3Cl$. Calculated %: N 12.37.

The hydrochloride is colorless. Recrystallized from anhydrous alcohol with the addition of ether. M.p. 126-128°. Readily soluble in water.

4.800 mg sub.: 0.402 ml N_2 (25°, 748 mm). 4.515 mg sub.: 0.382 ml N_2 (25°, 751 mm). Found %: N 9.44, 9.58. $C_{20}H_{24}N_3Cl_3 \cdot 2H_2O$. Calculated %: N 9.36.

7-Chloro-4-(3'-diethylaminomethyl-4'-hydroxyphenyl)aminoquinoline (II)

2-Hydroxy-5-acetaminobenzyldiethylamine (2.36 g) was boiled with 20% hydrochloric acid (5 ml) for 1 hour. The cooled liquid was neutralized with 10% sodium hydroxide solution, after which the solution was made weakly acid by the addition of concentrated hydrochloric acid. Then 4,7-dichloroquinoline (2 g) was added, and the reaction mass was heated on the boiling water bath for 2 hours. After cooling, the viscous yellow brown liquid was made alkaline with aqueous ammonia, and the obtained greenish gray solid was extracted with chloroform. The chloroform solution was washed with water and then dried over potash. Part of the chloroform was removed by distillation, after which alcoholic hydrochloric acid was added to the residue. The resulting hydrochloride separated as an oil, which congealed on rubbing. Yield 3.6 g (80%). Recrystallized from aqueous acetone as thin needles, m.p. 183-184°.

The yellow hydrochloride is extremely soluble in water and alcohol, insoluble in ether and acetone.

3.396 mg sub.: 0.294 ml N_2 (27°, 743 mm). 4.810 mg sub.: 0.412 ml N_2 (25°, 743 mm). Found %: N 9.63, 9.59. $C_{20}H_{24}O_2N_3Cl_3 \cdot H_2O$. Calculated %: N 9.41.

The base, obtained from the hydrochloride by treatment with aqueous ammonia, was recrystallized from anhydrous alcohol. Fine pale yellow needles, m.p. 207°. Readily soluble in alcohol, ether and acetone, insoluble in water; easily soluble in dilute acids, insoluble in alkalis. With ferric chloride gives a brown coloration.

2.193 mg sub.: 0.235 ml N_2 (27°, 743 mm). 4.007 mg sub.: 0.431 ml N_2 (25°, 743 mm). Found %: N 11.92, 12.04. $C_{20}H_{22}ON_3Cl$. Calculated %: N 11.81.

7-Chloro-4-(3'-diethylaminomethyl-4'-methoxyphenyl)aminoquinoline (III)

2-Methoxy-5-aminobenzyldiethylamine (2.5 g) and 4,7-dichloroquinoline (2.3 g) were heated in an oil bath at 160-170° for 12 hours. The cooled solid product was dissolved in 20 ml of 50% acetic acid, filtered, and alkalized with a 10% sodium hydroxide solution. The obtained base was filtered and washed with water. Yield 4.1 g (87%). Recrystallized from heptane; tiny needles, m.p. 201-202°. The light yellow base is soluble in alcohol, acetone and ether, insoluble in water and dilute alkali; easily soluble in dilute acids.

2.012 mg sub.: 0.211 ml N_2 (28°, 742 mm). 2.758 mg sub.: 0.294 ml N_2 (29°, 742 mm). Found %: N 11.61, 11.76. $C_{21}H_{24}ON_3Cl$. Calculated %: N 11.37.

* The melting point of the base agrees with the literature data [4]; the melting point of the hydrochloride is not given in the literature.

Yellow hydrochloride, m.p. 198-199° (decomposition). Readily soluble in water and alcohol, insoluble in ether and acetone.

3.845 mg sub.: 0.323 ml N_2 (30°, 743 mm). 3.764 mg sub.: 0.313 ml N_2 (30°, 743 mm). Found %: N 9.25, 9.15. $C_{21}H_{26}ON_3Cl_3 \cdot H_2O$. Calculated %: N 9.12.

7-Chloro-4-(4'-hydroxyphenyl)aminoquinoline

To a solution of p-aminophenol sulfate (7.9 g) in water (45 ml) was added 4,7-dichloroquinoline (9.9 g), and the liquid was heated on the boiling water bath for 3 hours with stirring. The reaction mass quickly changed into a thick yellow slurry, which was filtered and treated with aqueous ammonia. Yield quantitative, m.p. 255-256°, which agrees with the literature [5].

7-Chloro-4-[3',5'-bis(diethylaminomethyl)-4'-hydroxyphenyl]-aminoquinoline (V)

a) 3,5-bis(Diethylaminomethyl)-4-hydroxyacetanilide (3.2 g) was boiled with 20% hydrochloric acid (5 ml) for 1 hour. The liquid was neutralized with 10% sodium hydroxide solution, made weakly acid by the addition of concentrated hydrochloric acid, and then heated with 4,7-dichloroquinoline (2 g) for 2 hours on the boiling water bath with stirring of the reaction mixture. After cooling, the solution was made alkaline with aqueous ammonia and then extracted with ether. The ether solution was washed with water and dried over potash. After removal of the solvent by distillation there remained 4 g (89%) of base, which was recrystallized from acetone, from petroleum ether, or from a mixture of benzene and petroleum ether. Tiny needles, m.p. 162-163°. The yellow base is readily soluble in benzene, acetone, alcohol and ether, difficultly soluble in petroleum ether, insoluble in water; easily soluble in dilute acids, insoluble in dilute alkalis. With ferric chloride gives a brown coloration.

5.457 mg sub.: 0.578 ml N_2 (22°, 762 mm). 4.034 mg sub.: 0.431 ml N_2 (21°, 760 mm). Found %: N 12.29, 12.40. $C_{25}H_{33}ON_4Cl \cdot 0.75\ H_2O$. Calculated %: N 12.33.

The highly hygroscopic yellow hydrochloride is extremely soluble in water and alcohol. Analysis of the hydrochloride was made after reduction to constant weight.

3.900 mg sub.: 0.353 ml N_2 (22°, 754 mm). 5.532 mg sub.: 0.510 ml N_2 (24°, 756 mm). Found %: N 10.39, 10.54. $C_{25}H_{35}ON_4Cl_4$. Calculated %: N 10.18.

Lemon yellow oxalate. M.p. 154-155° (decomposition). Readily soluble in water.

6.560 mg sub.: 0.490 ml N_2 (22°, 745 mm). 4.904 mg sub.: 0.363 ml N_2 (23°, 746 mm). Found %: N 8.47, 8.38. $C_{25}H_{33}ON_4Cl \cdot 1.5\ H_2C_2O_4 \cdot 5H_2O$. Calculated %: N 8.42.

b) 7-Chloro-4-(4'-hydroxyphenyl)aminoquinoline (8.1 g), formalin (7 ml), diethylamine (45 ml) and alcohol (30 ml) were heated at the boil in a flask on the water bath for 6 hours. On conclusion of heating, the alcohol and excess diethylamine were removed by distillation, the residue was dissolved in 10% hydrochloric acid and boiled with charcoal, filtered, and made alkaline with aqueous ammonia. The obtained grayish product was extracted with ether: 0.8 g of substance failed to dissolve. The ether solution was washed with ether and dried over potash.

The residue after the removal of solvent by distillation was repeatedly extracted with ether, in which connection another 0.2 g of substance failed to dissolve. After distilling off the solvent there remained 9.8 g (76%) of solid base, which was recrystallized from acetone or from a mixture of benzene and petroleum ether. M.p. 162-163°; no depression of the melting point was observed when this compound was mixed with the 7-chloro-4-[3',5'-bis(diethylaminomethyl)-4'-hydroxyphenyl]-aminoquinoline obtained by the first method. The substance, insoluble in ether, after recrystallization from aqueous acetone, melted at 183-184° and proved to be 7-chloro-4-(3'-diethylaminomethyl-4'-hydroxyphenyl)aminoquinoline.

c) 7-Chloro-4-(3'-diethylaminomethyl-4'-hydroxyphenyl)-aminoquinoline (3.5 g), formalin (1 ml), diethylamine (4 ml) and alcohol (5 ml) were heated on the boiling water bath for 6 hours. Further treatment was the same as in the preceding experiment. The product was recrystallized from a benzene-petroleum ether mixture, m.p. 160-162°. No depression of the melting point was observed when the compound was mixed with the compounds obtained by methods (a) and (b).

7-Chloro-4-(3'-diethylaminomethylsaligeninmethylene ether)-aminoquinoline (IV)

To a solution of the hydrochloride of 3-diethylaminomethyl-5-aminosaligeninmethylene ether (3 g) in water (5 ml) was added 2 g of 4,7-dichloroquinoline, and the reaction mass was heated with stirring on the boiling water bath for 2 hours. After cooling, the viscous yellow liquid was made alkaline with aqueous ammonia and then extracted with chloroform; the chloroform solution was washed with water and dried over potash. After distilling off

the solvent there remained 3 g (75%) of the base, which was recrystallized from aqueous acetone and from benzene. Long thin needles, m.p. 177°. The light yellow base is readily soluble in water; easily soluble in dilute acids.

4.470 mg sub.: 0.421 ml N_2 (30°, 742 mm). 4.848 mg sub.: 0.460 ml N_2 (30°, 739 mm). Found %: N 10.35, 10.39. $C_{22}H_{24}O_2N_3Cl$. Calculated %: N 10.57.

The yellow oxalate was recrystallized from methyl alcohol. Stout needles, m.p. 198° (decomposition). Readily soluble in water.

2.435 mg sub.: 0.196 ml N_2 (30°, 739 mm). 2.963 mg sub.: 0.235 ml N_2 (30°, 739 mm). Found %: N 8.81, 8.68. $C_{24}H_{26}O_6N_3Cl$. Calculated %: N 8.61.

7-Chloro-4-(3'-diethylaminomethyl-4'-hydroxy-5'-hydroxymethylphenyl)-aminoquinoline (VI)

3-Diethylaminomethyl-4-hydroxy-5-hydroxymethylaniline (2.2 g) and 4,7-dichloroquinoline (2 g) were heated under slightly acid conditions with stirring on the boiling water bath for 2 hours. The solution was made alkaline with aqueous ammonia. The obtained base was converted into the picrate, which was recrystallized from aqueous acetone. M.p. 162-164° (decomposition).

4.367 mg sub.: 0.519 ml N_2 (22°, 758 mm). 4.349 mg sub.: 0.519 ml N_2 (18°, 755 mm). Found %: N 13.72, 13.91. $C_{27}H_{27}O_9N_6Cl$. Calculated %: N 13.67.

SUMMARY

1. A number of new quinoline compounds with side chain cyclic substituents were synthesized and characterized: the substituents being m-aminobenzyldiethylamine and its derivatives, attached to the ring at the 4-position through the NH group.

2. The antimalarial activity of the synthesized compounds exceeds the activity of chloroquine, in certain cases being 3-4 times as active as chloroquine and 10 times as active as atebrin; the toxicity is below the toxicity of chloroquine.

3. The introduction of hydroxy and methoxy groups into the side chain cyclic substituent significantly raises the antimalarial activity, which is sharply increased in the presence of a second, symmetrically arranged, diethylamino group.

4. A method for the separation of mixtures of monobasic and dibasic Mannich compounds by fractional treatment with ether has been developed.

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* See Consultants Bureau Translation, page 177.

CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

XVI. 8-ARYLAMINOQUINOLINES

V. I. Stavrovskaya

The earlier described antimalarial compounds of the acridine and quinoline series with side chain cyclic substituents revealed both a higher activity and a lower toxicity than the corresponding compounds possessing aliphatic amines [1, 2].

This circumstance made us believe that the introduction of cyclic substituents in the eight-position of 6-methoxy-8-aminoquinoline would lead to active antimalarial compounds with a lower toxicity than that possessed by plasmochin and plasmocid, and is the subject of the present investigation.

In the synthesis of these compounds we encountered a number of experimental difficulties.

At the present time, the methods for the introduction of alkyl groups and, especially, of dialkylaminoalkyl groups into 8-aminoquinolines have been well-developed [3, 4], and with their aid a large number of 8-(dialkylaminoalkyl)aminoquinolines have been synthesized, in which connection, some of them have found extensive use in practice for the treatment of malaria (plasmocid, plasmochin).

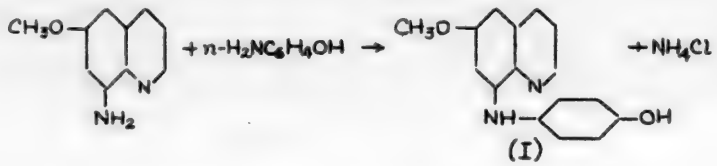
Methods for the introduction of aryl groups in 8-aminoquinolines have been investigated only in isolated cases: 8-(2,4-dinitrophenol)aminoquinoline was obtained by heating alcoholic solutions of 8-aminoquinoline and 2,4-dinitrochlorobenzene or by their fusion [5]. However, the necessary presence of the nitro group, attached in definite positions, limits the use of this method; 8-(4'-hydroxyphenyl)- and 8-(4'-aminophenyl)aminoquinoline were synthesized by the Bucherer reaction from 8-hydroxyquinoline and p-aminophenol or p-phenylenediamine [6]. As was shown by Chelintsev and Dubinin in the case of aliphatic amines, this reaction fails to proceed when a substituent is present in the 6-position of the quinoline nucleus [7] and, consequently, possesses limited application.

We attempted to realize the synthesis of 8-arylaminoquinolines by several methods: through o-nitrodiphenylamine with subsequent reduction of the nitro group and running a Skraup synthesis on the obtained o-aminodiphenylamine; from 8-hydroxyquinoline by the Bucherer reaction; by the direct arylation of 8-aminoquinoline. We obtained the o-nitrodiphenylamine needed for the synthesis either through replacement of the aromatic halogen in o-nitrochlorobenzene or of the labile nitro group in o-dinitrobenzene by the aromatic amine. However, the low yields in the first stage of the synthesis — the replacement of aromatic halogen by the aromatic amine — caused us to reject this method and to go over to the second method — making use of the labile nitro group in o-dinitrobenzene. The method for the condensation of o-dinitrobenzene with aliphatic and aromatic amines served as the basis for this [8-10]. o-Dinitrobenzene was heated with m-aminobenzyldiethylamine; the obtained 1-nitro-3'-diethylaminodiphenylamine was reduced and subjected to the Skraup synthesis. 8-(3'-Diethylaminomethylphenyl)-aminoquinoline and 8-(4'-diethylaminomethylphenyl)aminoquinoline were obtained in this manner. The method had a number of disadvantages: difficulty in obtaining o-dinitrobenzene, losses during reduction and, especially, losses during the Skraup synthesis; impossibility of obtaining the 4-hydroxyphenyl derivative, since in this case the hydrogen of the hydroxyl group is the chief reactant.

Our attempts to introduce the aryl residue into 8-aminoquinoline by the Bucherer reaction [7] led to unsatisfactory results. Only the starting 8-hydroxyquinoline and m-aminobenzyldiethylamine were isolated from the reaction mass.

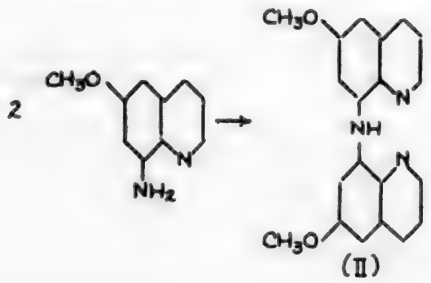
We developed a method for the preparation of 6-methoxy-8-(4'-hydroxyphenyl)aminoquinoline, which consisted in the heating of a mixture of the hydrochloride (or base) of 6-methoxy-8-aminoquinoline with the free (or hydrochloride) p-aminophenol in a sealed tube at 185-190° for 5 hours.

The reaction is complicated by the formation of secondary products, since, in addition to the basic substance 6-methoxy-8-(4'-hydroxyphenyl)aminoquinoline (I), obtained in 35-40% yield:



(I)

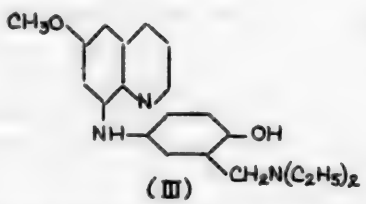
small amounts of 4,4 -dihydroxydiphenylamine and 6-methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline* (II) are obtained:



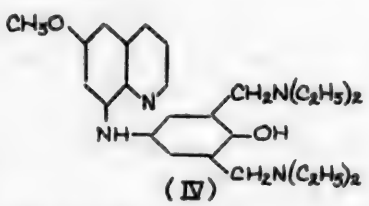
(II)

In addition to the above enumerated compounds, we isolated from the reaction product a considerable amount (about 40% by weight) of hard black substance with m.p. around 300°. The structure of this substance was not established.

From the obtained 6-methoxy-8-(4'-hydroxyphenyl)aminoquinoline via the Mannich reaction with formaldehyde and diethylamine we synthesized 6-methoxy-8-(3'-diethylaminomethyl-4'-hydroxyphenyl)aminoquinoline (III) and 6-methoxy-8-[3',5'-bis(diethylaminomethyl)-4'-hydroxyphenyl]aminoquinoline (IV):



(III)



(IV)

The mixture of compounds (III) and (IV) was separated on the basis of their different solubility in ether, analogous to the solubility of the mono- and dibasic Mannich compounds of the acridine and 4-aminoquinoline series, which we described earlier. The bases of the products synthesized by us are light brown solids, gradually darkening on standing in the air. The hydrochlorides are brown solids, readily soluble in water.

When biologically tested for antimalarial activity these compounds were found to possess neither gamotropic nor schizotropic activity.**

EXPERIMENTAL

2-Nitro-4'-diethylaminomethyldiphenylamine. The well-ground mixture of o-dinitrobenzene (4 g) and p-aminobenzyldiethylamine (3 g) was heated in a small flask with vertical tube in an oil bath. At 110° fine bubbles began to appear on the surface of the liquid, at 140-145° steady boiling began. This temperature was maintained for 10 hours. After cooling, the reaction product was rubbed in a mortar with 10% hydrochloric acid. The hydrochloric acid solution was made alkaline with 10% sodium hydroxide solution, and the obtained dark viscous substance was extracted with ether. The ether solution was dried over potash. After distilling off the ether there remained 3.7 g of dark red liquid, which decomposed when vacuum distillation was attempted. The picrate,

* We also obtained 6-methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline by heating molal amounts of the free 6-methoxy-8-aminoquinoline and its hydrochloride.

** We wish to thank Prof. Sh. D. Moshkovsky and S. A. Syrkina for making the biological studies.

obtained by mixing alcohol solutions of the free base and picric acid, was recrystallized from alcohol. Needles, m.p. 85-87°.

3.917 mg sub.: 0.549 ml N_2 (16°, 738 mm). 5.466 mg sub.: 0.774 ml N_2 (18°, 738 mm). Found %: N 16.08, 16.11. $C_{23}H_{24}O_9N_6$. Calculated %: N 15.91.

2-Amino-4'-diethylaminomethyldiphenylamine. 2-Nitro-4'-diethylaminomethyldiphenylamine (3 g) was dissolved in concentrated hydrochloric acid (11 ml) and to this solution was gradually added a solution of stannous chloride (9.7 g) in concentrated hydrochloric acid; in this connection a small amount of heat evolution was observed. The nitro compound, compacted into a clod at the start of addition, gradually became thinner. After all of the stannous chloride solution had been added, the reaction mass was allowed to stand at room temperature for 2 hours. Then a 40% sodium hydroxide solution was added, and the liquid was repeatedly extracted with ether. The ether solution was dried over potash. After removal of the solvent, there remained 2.5 g of mobile red oil (diazotizes and couples with β-naphthol). The picrate was prepared from the obtained base. The picrate was purified by recrystallization from water, hexagonal plates, m.p. 128°.

1.874 mg sub.: 0.284 ml N_2 (20°, 741 mm). 1.900 mg sub.: 0.284 ml N_2 (17°, 741 mm). Found %: N 17.21, 17.16. $C_{29}H_{29}O_{14}N_9$. Calculated %: N 17.33.

8-(4'-Diethylaminomethylphenyl)aminoquinoline. 2-Amino-4'-diethylaminomethyldiphenylamine (4.3 g, not purified after reduction) was subjected to the Skraup synthesis, for which the amine was mixed with glycerol (7 ml); to this was gradually added concentrated sulfuric acid (5 ml) and nitrobenzene (2.5 ml). The mixture was heated; after some time a vigorous reaction set in, on the conclusion of which boiling of the liquid was continued for another 4 hours. After cooling, the reaction mixture was poured into an approximately equal amount of water and allowed to stand overnight. A tar deposited on the sides of the flask. The acid solution was extracted three times with ether to remove residual nitrobenzene and was then made alkaline with 10% sodium hydroxide solution. The obtained tarlike mass was dissolved in 10% hydrochloric acid, boiled with charcoal, filtered, and made alkaline a second time. The dark brown product obtained in this manner was purified again by boiling the acid solution with charcoal, after which it was filtered, made alkaline, and extracted with ether. The ether solution was dried over potash. After distilling off the ether there remained 0.8 g of light viscous liquid, which on standing acquired the consistency of vaseline. The picrate was prepared from the obtained base, and was recrystallized from water in the form of leaflets. From alcohol it is obtained as plates, m.p. 216°.

4.260 mg sub.: 0.627 ml N_2 (19°, 739 mm). 5.267 mg sub.: 0.784 ml N_2 (21°, 730 mm). Found %: N 16.73, 16.61. $C_{32}H_{29}O_{14}N_9$. Calculated %: N 16.51.

2-Nitro-3'-diethylaminomethyldiphenylamine. A mixture of o-dinitrobenzene (5.9 g) and m-aminobenzyldiethylamine (18.7 g) was heated on the boiling water bath for 11 hours. On conclusion of heating, the reaction mixture was a dark brown viscous liquid, which was made alkaline with 10% sodium hydroxide solution and extracted with ether. The ether solution was dried over potash. The residue after removal of the solvent was vacuum distilled; 9.6 g of unreacted amine was obtained with b.p. 112-120° at 3-4 mm. The residue in the flask was dissolved in 10% hydrochloric acid and filtered from a small amount of o-dinitrobenzene (0.45 g). The filtrate was made alkaline and the resulting viscous dark brown mass was extracted with ether. After distilling off the ether there remained 8.4 g of heavy liquid. The picrate, obtained by mixing alcohol solutions of the base and picric acid, was recrystallized from alcohol, m.p. 142°.

5.720 mg sub.: 0.809 ml N_2 (18°, 744 mm). 4.087 mg sub.: 0.574 ml N_2 (18°, 744 mm). Found %: N 16.24, 16.13. $C_{22}H_{24}O_9N_6$. Calculated %: N 15.91.

2-Amino-3'-diethylaminomethyldiphenylamine. 2-Nitro-3'-diethylaminomethyldiphenylamine (11.8 g, not purified) was reduced with stannous chloride in hydrochloric acid. The picrate was prepared from the base 2-amino-3'-diethylaminomethyldiphenylamine, and was recrystallized from water. Needles, m.p. 160-161°.

5.016 mg sub.: 0.764 ml N_2 (24°, 745 mm). 3.775 mg sub.: 0.588 ml N_2 (25°, 744 mm). Found %: N 17.16, 17.47. $C_{29}H_{29}O_{14}N_9$. Calculated %: N 17.33.

8-(3'-Diethylaminomethylphenyl)-aminoquinoline. 2-Amino-3'-diethylaminomethyldiphenylamine (6 g, not purified after reduction) was mixed with glycerol (10 ml); to this was gradually added concentrated sulfuric acid (7 ml) and nitrobenzene (4 ml). The mixture was charged into a flask and heated on the gauze. On conclusion of vigorous reaction, the liquid was boiled another 4 hours. Further treatment was the same as for the preparation of 8-(4'-diethylaminomethylphenyl)aminoquinoline. 1.4 g of the base was obtained, as a viscous liquid, from which the picrate was prepared. Recrystallized from alcohol, stout needles, m.p. 204-205°.

4.780 mg sub.: 0.706 ml N_2 (24°, 744 mm). 4.819 mg sub.: 0.706 ml N_2 (24°, 744 mm). Found %: N 16.62, 16.48. $C_{22}H_{20}O_4N_2$. Calculated %: N 16.51.

Attempts to prepare 8-(3'-diethylaminomethylphenyl)aminoquinoline by the Bucherer reaction. m-Aminobenzyldiethylamine (6.7 g) and water (20 ml) were charged into a small flask, into which sulfur dioxide gas was then passed to a weight increase of 2.6 g; the oil thus obtained, at first floating on the surface, gradually dissolved and the solution acquired a reddish color. The 8-hydroxyquinoline was then added and the liquid was boiled for 30 hours under slight pressure (mercury seal 10 cm). On conclusion of heating, a yellow substance deposited in the cooled solution, which was filtered. Yield 0.9 g, m.p. 72-73°.

The clear solution was made alkaline with 10% sodium hydroxide solution until an oil layer appeared on the surface, after which the oil was extracted with ether. The ether solution was dried over potash. After distilling off the ether, there remained 6.2 g of yellow liquid, which distilled at 123-124° (3-4 mm), corresponding to starting m-aminobenzyldiethylamine. Yield 4.5 g. The aqueous alkaline residue remaining after ether extraction was neutralized with 10% hydrochloric acid. The obtained flocculent precipitate was filtered and washed with water. Yield 1.2 g, m.p. 70-72°. The product was combined with the first portion of solid substance and steam distilled. Fine white needles, m.p. 75°.

The mixed melting point with 8-hydroxyquinoline remained unchanged. Therefore, only the original substances were isolated from the reaction mass.

6-Methoxy-8-(4'-hydroxyphenyl)aminoquinoline. A mixture of 6-methoxy-8-aminoquinoline hydrochloride (25.2 g) and free p-aminophenol (13.2 g) was intimately ground in a mortar, after which it was heated in a sealed tube for 5 hours at 185-190°. On conclusion of heating, the black melt was extracted several times with boiling water; then the cooled product was ground in a mortar with aqueous ammonia, filtered, and repeatedly extracted with ether (a considerable portion of the product failed to go into solution). The ether solution was washed with water and then dried over potash. After distilling off the ether there remained a black viscous and sticky mass, which was treated a second time with ether, and again a certain amount of dark product was obtained. This operation of dissolving the substance in ether was repeated several times. After distilling off the ether, the sticky black residue was covered with aqueous ammonia, the substance gradually solidified and, on crushing, had a greenish gray color. The substance was filtered, washed with water, and dried. Yield 12.2 g (38%).

On standing in the air, it rapidly darkened and turned balck. Recrystallized from benzene. After several recrystallizations, the substance was dark yellow; however, even on standing in a vacuum desiccator, it begins to turn green at first, and then becomes dark colored. M.p. 110-112° with incipient decomposition, vigorous decomposition at 118-120°. The base is readily soluble in alcohol, ether and benzene, soluble in dilute alkalis, soluble in 10% hydrochloric acid on heating, insoluble in water.

6.273 mg sub.: 0.598 ml N_2 (22°, 744 mm). 4.018 mg sub.: 0.382 ml N_2 (22°, 755 mm). Found %: N 10.80, 10.93. $C_{16}H_{14}O_2N_2$. Calculated %: N 10.53.

The picrate was prepared by mixing alcohol solutions of the base and picric acid. Recrystallized from alcohol, m.p. 169-170° (decomposition).

2.510 mg sub.: 0.314 ml N_2 (25°, 757 mm). 3.101 mg sub.: 0.392 ml N_2 (27°, 748 mm). Found %: N 14.27, 14.15. $C_{22}H_{17}O_9N_5$. Calculated %: N 14.14.

From the aqueous solution, obtained in the extraction of the melt with boiling water, very small amounts of 4,4'-dihydroxydiphenylamine, p-aminophenol and 6-methoxy-8-aminoquinoline were isolated. From the product, insoluble in ether, there was extracted with benzene 1.8 g of 6-methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline with m.p. 167-169° after purification.

The black substance, insoluble in ether and benzene (about 40% by weight), melts around 300°.

6-(Methoxy-8-(3'-diethylaminomethylphenyl)aminoquinoline and 8-[3'-5'-bis(diethylaminomethyl)-4'-hydroxyphenyl]aminoquinoline. 6-Methoxy-8-(4'-hydroxyphenyl)aminoquinoline (8.5 g), formalin (7 ml), diethylamine (30 ml) and absolute alcohol (30 ml) were heated in a flask under reflux for 5 hours. On conclusion of reaction, the alcohol and excess diethylamine were distilled off. The residue, a viscous brown liquid, was dissolved in 10% hydrochloric acid. The hydrochloric acid solution was boiled with charcoal, filtered, and made alkaline with aqueous ammonia. The obtained dark red substance was extracted with ether, with part of the substance failing to go into solution (6.1 g of dark red product).

a) The ether solution was washed with water and then dried over potash. After distilling off the ether, there remained 6 g of liquid mass, which solidified on cooling. The base was treated with alcoholic hydrochloric acid,

followed by the addition of dry acetone. The obtained solid hydrochloride was purified by dissolving it in methyl alcohol and then adding acetone. The dark orange hydrochloride is readily soluble in water and alcohol, insoluble in ether and acetone; m.p. 200-202° (decomposition).

3.184 mg sub.: 0.284 ml N_2 (21°, 751 mm). 6.135 mg sub.: 0.549 ml N_2 (24°, 757 mm). Found %: N 10.23, 10.24. $C_{28}H_{38}O_2N_4Cl_2 \cdot 3H_2O$. Calculated %: N 9.95.

The yellow base was obtained from the hydrochloride by treating the latter with aqueous ammonia. Extremely soluble in ethyl acetate, acetone, chloroform and ethylene dichloride; readily soluble in ether, difficultly soluble in petroleum ether; insoluble in water and dilute alkali, easily soluble in 10% hydrochloric acid. With ferric chloride gives a brown coloration Purified by recrystallization from aqueous alcohol. M.p. 110-112° (decomposition).

5.409 mg sub.: 0.617 ml N_2 (20°, 739 mm). 4.452 mg sub.: 0.510 ml N_2 (19°, 738 mm). Found %: N 12.92, 13.00. $C_{28}H_{36}O_2N_4$. Calculated %: N 12.84.

b) The ether insoluble substance was heated with ethyl acetate (about one-third of the product failed to dissolve). After the solvent was distilled off, there remained a dark red solid, which was purified by repeated solution in acetone and precipitation with water, or by solution in benzene and precipitation with petroleum ether; m.p. 188-190° (gradual decomposition). The base is readily soluble in acetone, soluble in alcohol, difficultly soluble in ether, and insoluble in water. The aqueous-alcohol solution of the base gives a brown coloration with ferric chloride.

5.271 mg sub.: 0.539 ml N_2 (20°, 750 mm). 2.840 mg sub.: 0.294 ml N_2 (21°, 750 mm). 2.989 mg sub.: 7.815 mg CO_2; 1.919 mg H_2O. 3.111 mg sub.: 8.165 mg CO_2; 1.956 mg H_2O. Found %: N 11.76, 11.86; C 71.35, 71.62; H 7.18, 7.03. $C_{21}H_{25}O_2N_3$. Calculated %: N 11.97; C 71.80; H 7.18.

The light brown hydrochloride is readily soluble in water.

5.007 mg sub.: 0.431 ml N_2 (22°, 741 mm). 4.679 mg sub.: 0.402 ml N_2 (22°, 741 mm). Found %: N 9.71. 9.69. $C_{21}H_{28}O_2N_3Cl \cdot 3H_2O$. Calculated %: N 9.51.

6-Methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline. The free 6-methoxy-8-aminoquinoline (7 g) and its hydrochloride (8.4 g) were well-mixed and then heated in a sealed tube for 11 hours at 170-175°. The obtained black melt was rubbed in a mortar with aqueous ammonia, filtered, washed with water, and dried. The impure product had m.p. 80-90° (decomposition). To remove unreacted 6-methoxy-8-aminoquinoline, the substance was repeatedly shaken and rubbed with ether; after distilling off the ether, there remained 5.1 g of 6-methoxy-8-aminoquinoline. The product, insoluble in ether (7.3 g), melted at 125-135° (decomposition). Recrystallized from a mixture of benzene and petroleum ether. Microcrystals with m.p. 168-170 (ill-defined).

The dark yellow base is soluble in alcohol, acetone, benzene, ethyl acetate and dilute hydrochloric acid; difficultly soluble in petroleum ether, insoluble in water and dilute alkali.

3.933 mg sub.: 0.451 ml N_2 (22°, 741 mm). 3.193 mg sub.: 0.363 ml N_2 (21°, 742 mm). Found %: N 12.94, 12.89. $C_{19}H_{17}O_2N_3$. Calculated %: N 12.69

Treatment of the base with alcoholic hydrochloric acid and subsequent addition of ether gives the yellow hydrochloride. Soluble in alcohol, difficultly soluble in water, readily hydrolyzed on heating with water. The hydrochloride was purified by dissolving in methyl alcohol with the subsequent addition of ether. Decomposes at 287-290°.

6.768 mg sub.: 0.706 ml N_2 (28°, 748 mm). 5.602 mg sub.: 0.578 ml N_2 (28°, 748 mm). Found %: N 11.64, 11.52. $C_{20}H_{19}O_2N_3Cl$. Calculated %: N 11.43.

As a result, the analysis of the base and its hydrochloride identify the substance as being 6-methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline.

SUMMARY

1. A number of new 8-arylaminoquinolines, where the aryl is 4-hydroxyphenyl-3-diethylaminomethylphenyl, 4-diethylaminomethylphenyl, 3-diethylaminomethyl-4-hydroxyphenyl and 3,5-bis-diethylaminomethyl-4-hydroxyphenyl, were synthesized and characterized.

2. When investigated for avian malaria infection substances (III) and (IV) proved to be inactive.

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• See Consultants Bureau Translation, page 177.

•• See Consultants Bureau Translation, page 317.

OXIDATION OF ω-ACETOXYHEXAHYDROACETOPHENONE

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It is known that ketones can be oxidized by different oxidizing agents like, for example, chromic acid, nitric acid, potassium permanganate, etc., the oxidation results depending both on the structure of the ketone and, to a considerable degree, on the oxidizing agent used. The α-hydroxy ketones are especially susceptible to oxidation [1].

We obtained extremely interesting results when ω-acetoxyhexahydroacetophenone (I) [2, 9] was exposed to the action of a mild oxidizing agent like silver oxide in alkaline medium. It was revealed that the oxidation of this compound under the indicated conditions proceeds very easily, even the development of a certain amount of heat being observed. Two acids were obtained as a result of the reaction, the liquid acid being readily soluble in benzene, while the solid acid was found to be practically insoluble in cold benzene.

From the acid soluble in benzene we obtained the amide, m.p. 186-187°. Analysis of this amide revealed that it was saturated and that it corresponds to an acid with empirical formula $C_7H_{12}O_2$, i.e., apparently, to hexahydrobenzoic acid (II).

$C_6H_{11}-CO-CH_2OCOCH_3$, (I) $C_6H_{11}-COOH$, (II) $C_6H_{11}-CHOH-COOH$ (III)

From the literature, the amide of hexahydrobenzoic acid has m.p. 184° [3] and 185-186° [4]. The amide of hexahydrobenzoic acid synthesized by us had m.p. 186.5-187.5° and no depression of the melting point was observed when this amide was mixed with the amide obtained from the benzene-soluble liquid acid. As a result, it was shown that one of the acids obtained in the oxidation of ω-acetoxyhexahydroacetophenone is hexahydrobenzoic acid (II).

The acid difficultly soluble in benzene, obtained in much smaller amount (approximately $^1/_5$ of the amount of hexahydrobenzoic acid), after recrystallization had m.p. 134.5-135°. Analysis of this acid revealed its empirical formula to be $C_8H_{14}O_3$; its equivalent weight, determined by titration, was found to be 158. The amount of labile hydrogen in this compound indicated the presence of 2 hydroxyl groups. From this data it can be concluded that the acid with m.p. 134.5-135 is hexahydromandelic acid (III) (from the literature, m.p. 135-136°, 130-131° [5]).

Conclusive evidence for the identity of the solid acid (m.p. 134.5-135°) with hexahydromandelic acid was obtained by the method of synthesizing the latter from benzaldehyde and HCN with subsequent hydrolysis of the thus obtained cyanohydrin [5]. No depression of the melting point was observed when hexahydromandelic acid was mixed with the solid acid (m.p. 134.5-135°) obtained from the oxidation of ω-acetoxyhexahydroacetophenone.

At first glance, the formation of hexahydromandelic acid in this reaction is completely unexpected, inasmuch as under the conditions of this oxidation process the >C=O group is reduced to >CHOH. However, under more careful examination, this unique reaction can be fully explained. Probably, the first reaction that takes place in the alkaline medium is hydrolysis of the acetoxy group; the resulting α-keto alcohol (IV) is oxidized to the α-keto aldehyde (V) (cyclohexylglyoxal), while the cyclohexylglyoxal in alkaline medium is rearranged into hexahydromandelic acid (III), analogous to the Cannizzaro reaction or to the benzilic acid type of rearrangement. Examples of a similar type of intramolecular disproportionation are known, for example, for methylglyoxal [6] and phenylglyoxal [7].

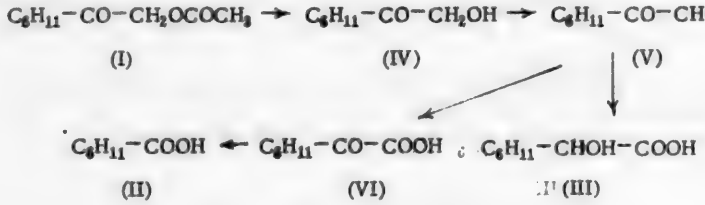
Two theories can be offered to explain the formation of hexahydrobenzoic acid in this reaction: the oxidation of the hexahydromandelic acid formed in the reaction to hexahydrobenzoic acid (Scheme A) or the oxidation of the intermediate cyclohexylglyoxal to hexahydrobenzoylformic acid (VI), which is then converted into hexahydrobenzoic acid (Scheme B):

$$C_6H_{11}-CO-CHO \longrightarrow C_6H_{11}-CHOH-COOH \longrightarrow C_6H_{11}-COOH \quad (A)$$
(V) (III) (II)

$$C_6H_{11}-CO-CHO \longrightarrow C_6H_{11}-CO-COOH \longrightarrow C_6H_{11}-COOH \quad (B)$$
(V) (VI) (II)

In order to give preference to one of these schemes, it was necessary to determine if hexahydromandelic acid under the experimental conditions is oxidized to hexahydrobenzoic acid. It was revealed that pure hexahydromandelic acid remains completely unchanged when it is exposed to the action of silver oxide in alkaline medium. From this it follows that the formation of hexahydrobenzoic acid probably proceeds in accord with Scheme B.

As a result, the complete oxidation of ω-acetoxyhexahydroacetophenone under the indicated conditions apparently proceeds as follows:



EXPERIMENTAL•

Oxidation of ω-acetoxyhexahydroacetophenone. To a solution of 1.54 g of ω-acetoxyhexahydroacetophenone (b.p. 103-104° at 2 mm, m.p. 42-43°) in 10 ml of alcohol was added 45 ml of water. To the resulting emulsion was added a solution of 8.42 g of silver nitrate in 14 ml of water and then in portions with stirring a solution of 1.9 g of sodium hydroxide in 17 ml of water was added. Some evolution of heat was observed. After all of the alkali had been added, the stirring was continued for another 30 minutes, after which the flask was heated on the water bath for 10 minutes. The precipitate was filtered and washed with hot water. The filtrate and wash liquors were extracted with ether to remove neutral impurities, after which the aqueous layer was acidified to Congo with dilute hydrochloric acid and then thoroughly extracted with ether. The ether solution was dried over anhydrous sodium sulfate.

After removal of the solvent, a mixture of acids was obtained, which partially crystallized on cooling. The mixture was treated with cold benzene and the benzene insoluble acid was filtered off. 0.17 g of crystalline acid was obtained which after recrystallization from benzene had m.p 134.5-135°. This acid is readily soluble in ether, alcohol, acetone, ethyl acetate and xylene, difficultly soluble in the cold in chloroform, benzene and water, and readily soluble in hot benzene.

4.145 mg sub.: 9.211 mg CO_2; 3.188 mg H_2O. 3.888 mg sub.: 8.655 mg CO_2; 3.063 mg H_2O. 1.42 mg sub.: 0.42 ml CH_4 (19°, 763 mm). 20.30 mg sub.: 1.30 ml 0.1 N NaOH. Found %: C 60.64, 60.74; H 8.60, 8.81; active H 1.25. M 156.1. $C_8H_{14}O_3$. Calculated %: C 60.74; H 8.91; active H 1.25. M 158.2.

After distilling the solvent from the benzene solution, there remained 0.8 g of liquid acid, which we were unable to crystallize. The substance was dissolved in dry benzene and the benzene solution was added in drops to a benzene solution containing 3.5 g of thionyl chloride. The mixture stood for 1 hour at room temperature and then was heated for 1 hour at 50-60°. After cooling, the excess thionyl chloride, together with the benzene, were removed by vacuum distillation at 20-25°. A stream of dry ammonia gas was passed into a flask containing dry benzene and at the same time a benzene solution of the obtained acid chloride was added dropwise. The obtained precipitate was filtered off and washed with water to remove ammonium chloride. The residue had m.p. 182°. After recrystallization from benzene, m.p. 186-187°. The substance is soluble in chloroform, alcohol and ethyl acetate, on heating – in benzene, practically insoluble in water, ether and acetone. A test with potassium permanganate solution revealed that the amide is a saturated compound.

3.816 mg sub.: 9.262 mg CO_2; 3.431 mg H_2O. 4.001 mg sub.: 9.731 mg CO_2; 3.617 mg H_2O. 7.103 mg sub.: 0.696 ml N_2 (21°, 742 mm). Found %: C 66.24, 66.37; H 10.06, 10.11; N 11.11. $C_7H_{13}ON$. Calculated %: C 66.11; H 10.30; N 11.02.

Hexahydrobenzoic acid (II) was obtained by the reduction of benzoic acid with metallic sodium, using the method described in the literature [3].

The amide of hexahydrobenzoic acid after recrystallization from hot water had m.p. 186.5-187.5°. No depression of the melting point was observed when this amide was mixed with the amide obtained from the liquid acid formed in the oxidation of ω-acetoxyhexahydroacetophenone.

• All melting points have been corrected.

Hexahydromandelic acid (III). To 3.4 g of freshly distilled hexahydrobenzaldehyde [8] was added a saturated solution of sodium bisulfite (55 ml). Stirring of the mixture was continued until it began to crystallize into a thick mass. The bisulfite compound was filtered off, washed with a small amount of ice water, after which it was mixed with a small amount of water, and to the obtained mixture with vigorous stirring was added a saturated solution containing 2 g of sodium cyanide. The reaction was complete after 20-30 minutes and the nitrile of hexahydromandelic acid separated as an oil. The nitrile was heated with a 4-fold amount of concentrated hydrochloric acid on the boiling water bath for 3 hours. The white crystalline substance obtained in this manner is the amide of hexahydromandelic acid. Yield 2.9 g. M.p. 166-167°. The substance is readily soluble in alcohol, on heating — in acetone, benzene and water; insoluble in ether.

The amide of hexahydromandelic acid (0.2 g) was heated on the boiling water bath with a slight excess of 10% aqueous potassium hydroxide solution for 2 hours. The deposit gradually dissolved. After cooling, the solution was acidified to Congo and exhaustively extracted with ether. Removal of the solvent from the dried ether extract gave 0.13 g of crystalline hexahydromandelic acid; after recrystallization from benzene, m.p. 134.5-135°. No depression of the melting point was observed when the acid with m.p. 134.5-135°, obtained in the oxidation of ω-acetoxyhexahydroacetophenone, was mixed with the authentic hexahydromandelic acid.

Attempt to oxidize hexahydromandelic acid with silver oxide in alkaline medium. Hexahydromandelic acid (0.17 g) was treated with silver oxide in alkaline medium under the same conditions as were used for the oxidation of ω-acetoxyhexahydroacetophenone, i.e., with heating of the reaction mixture for 10 minutes on the water bath and subsequent extraction with ether. After drying the ether solution and removal of the solvent, there remained 0.16 g of a dense crystalline mass, which proved to be pure original hexahydromandelic acid, melting without recrystallization at 129-130.5°. After recrystallization from benzene the m.p. rose to 134-135°.

SUMMARY

1. It was established that ω-acetoxyhexahydroacetophenone is readily oxidized by silver oxide in alkaline medium. The products of this reaction — hexahydrobenzoic and hexahydromandelic acids — were isolated and identified.

2. It was shown that hexahydrobenzoic acid is not an oxidation product of hexahydromandelic acid.

3. A probable scheme for the transformation of ω-acetoxyhexahydroacetophenone under the indicated conditions has been proposed.

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• See Consultants Bureau Translation, page 327 this issue.

STUDY OF THE TRANSFORMATION OF 1,1-PENTAMETHYLENEGLYCEROL 2,3-DIACETATE INTO ω-ACETOXYHEXAHYDROACETOPHENONE

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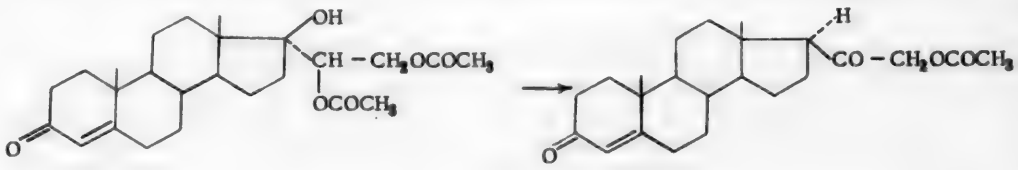
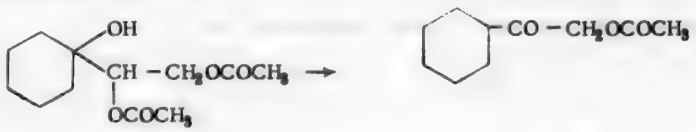
It has long been known that α-glycols and their acetyl derivatives can be transformed into aldehydes and ketones either under the influence of water-splitting agents or by heating them, most frequently with dilute acids[1].

In recent years this reaction has received extensive study in the sterol series where it has been used for the synthesis of biologically active compounds having the grouping $-CO-CH_2-R$ in their structure. The given process plays quite an essential role in the synthesis of the important steroid hormone – desoxycorticosterone (Δ^4-pregnen-21-ol-3,20-dione), and also for the preparation of other analogous ketones in the sterol series.

As a rule, the described reaction, usually called the Serini reaction in the literature, is operated by way of heating the corresponding diol, more frequently – its monoacetate, with zinc dust in an inert solvent at the boiling point of the latter. The preparation of desoxycorticosterone acetate from Δ^4 pregnene-17,20,21-triol-3-one, 20,21-diacetate can be depicted by the following scheme:



Inasmuch as the indicated synthesis almost always fails to proceed in a completely sstisfactory manner, and because unconditionally reliable data on the mechanism of the Serini reaction is missing in the literature, we set ourselves the task of studying this extremely interesting transformation on a comparatively simple and more accessible model. The model chosen by us was 1,1-pentamethyleneglycerol 2,3-diacetate (I) [2], from which ω-acetoxyhexahydroacetophenone (II) was obtained:



(I) (II)

The reaction was carried out by heating 1,1-pentamethyleneglycerol 2,3-diacetate in xylene with zinc dust, the acetic acid formed in the reaction being constantly removed from the reaction medium.

As the result of repeated distillations in vacuum (2 mm) we obtained the following fractions (the average yields of a number of experiments are given):

Fraction No.	Boiling Point	Amount (in % of the total weight of all fractions)
1	40-50°	1 - 2
2	78-95	5 - 8
3	95-100	1 - 3
4	105-110	45 - 50
5	112-116	6 - 8
6	126-135	30 - 40

The 4th fraction (b.p. 105-110° at 2 mm, m.p. 42-43°) is ω-acetoxyhexahydroacetophenone (II).*

Of especially great interest to us was establishment of the structure of the substances contained in the lower boiling fractions, inasmuch as this could be helpful in elucidating the mechanism of the process being studied.

Preliminary investigation revealed that the first 3 fractions, boiling from 40 to 100° (2 mm), show the reactions specific for aldehydes: the characteristic coloration with SO_2 decolorized fuchsin (Schiff's reagent), the formation of a silver mirror when treated in the cold with an ammoniacal silver oxide solution, and the deposition of yellow cuprous oxide when reacted in the cold with Fehling solution.

The character of the staining, obtained in the treatment with acid fuchsin (Schiff's reagent), was different for the 1st, 2nd and 3rd fractions: the 1st fraction gave an intense crimson, the 2nd fraction gave an intense violet, while the 3rd fraction gave a color analogous to the preceding but considerably weaker. Consequently, it could be assumed that different aldehydes are present in the 1st and 2nd fractions: the 3rd fraction, possibly, is a mixture of the aldehyde present in the 2nd fraction and ω-acetoxyhexahydroacetophenone (or some other compound, not possessing aldehyde properties).

For the sake of convenience the aldehyde from the 1st fraction in the future will be designated as aldehyde A, while the aldehyde from the 2nd fraction will be called aldehyde B. In asmuch as in the investigated reaction aldehyde B is obtained in considerably larger amount(5-8 % on the total amount of all of the fractions) than is aldehyde A (1-2%), we began to study the secondary products from this substance.

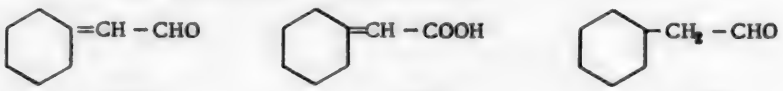
Analysis of the semicarbazone of aldehyde B (m.p. 208-209° with decompn.) revealed that aldehyde B has the empirical formula $C_8H_{12}O$. The analysis results for the 2,4-dinitrophenylhydrazone and thiosemicarbazone also support this formula.

It could be assumed that aldehyde B corresponds to one of the following structural formulas:

or as the result of possible displacement of the double bond the latter could also be found in some other part of the molecule.

Of the semicarbazones of the above depicted aldehydes, in the literature are described: the semicarbazone of cyclohexylideneacetaldehyde with m.p. 205° [4], 210° [5], and the semicarbazone of Δ^1-cyclohexeneacetaldehyde with m.p. 177° [5], 186° [4].

From this it follows that aldehyde B is apparently cyclohexylideneacetaldehyde (III). In addition, the ultraviolet absorption spectra taken of aldehyde B and its semicarbazone** had the same absorption bands as are given in the literature [4, 5] for cyclohexylideneacetaldehyde and its semicarbazone, and which are specifically characteristic for α,β-unsaturated carbonyl compounds (see experimental part).



(III) (IV) (V)

The oxidation of aldehyde B with silver oxide in alkaline medium gave two acids; one of them was crystalline (m.p. 91-92°; amide, m.p. 146.5-147.5°). These data completely agree with the melting points of cyclohexylideneacetic acid and its amide [6]. Mixtures of these substances with authentic cyclohexylideneacetic acid (IV) and its amide failed to show a melting point depression. The other acid, liquid, was isolated in extremely small amount (amide, m.p. 186-187°). We were unable to study this substance in greater detail.

The cyclohexylideneacetaldehyde (III) synthesized by us [5] gave with acid fuchsin (Schiff's reagent) the same intense violet color as aldehyde B. The semicarbazone (m.p. 208-209°) failed to give a melting point depression with the semicarbazone of aldehyde B.

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* In the literature [3] this substance is described as a liquid, which is possibly due to its being insufficiently pure.

** Yu. N. Sheinker participated in the study of the ultraviolet absorption spectra.

As the result of oxidizing pure cyclohexylideneacetaldehyde with silver oxide in alkaline medium we obtained only the pure cyclohexylideneacetic acid with a good melting point. Consequently, the liquid acid, whose amide had m.p. 186-187°, could not be obtained by the oxidation of cyclohexylideneacetaldehyde. In all probability it was present as the oxidation product of some substance, found as impurity in the given fraction in very small amounts (for more details on this acid see below).

As a result, it was shown that in the reaction for the transformation of 1,1-pentamethyleneglycerol 2,3-diacetate into ω-acetoxyhexahydroacetophenone the simultaneous formation of cyclohexylideneacetaldehyde also occurs.

Aldehyde A was obtained in extremely small amount when compared with the other substances. Judging from the analysis of its semicarbazone (m.p. 156-157°), aldehyde A has the empirical formula $C_8H_{14}O$, which differs from the formula for aldehyde B by only 2 hydrogen atoms. Proceeding from this, we postulated that aldehyde A is cyclohexylacetaldehyde (V), which was formed by the reduction of cyclohexylideneacetaldehyde. The latter is completely possible under the experimental conditions, inasmuch as in the reaction mixture together with the zinc dust there is always present some free acetic acid formed in the reaction process.

The literature data on the melting point of cyclohexylacetaldehyde semicarbazone are quite contradictory [8-12].

To demonstrate the identity of aldehyde A with cyclohexylacetaldehyde we hydrogenated the semicarbazone of the cyclohexylideneacetaldehyde at our disposal. The obtained semicarbazone of the saturated aldehyde had the same crystal form as the semicarbazone of aldehyde A, it melted at 157-158° and failed to give a melting point depression when mixed with the semicarbazone from aldehyde A.

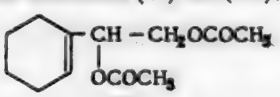
The 3rd fraction (b.p. 95-100° at 2 mm) failed to crystallize when seeded with ω-acetoxyhexahydroacetophenone and, possibly, is a mixture of the latter with aldehyde B.

Actually, the oxidation of the 3rd fraction with silver oxide in alkaline medium led to the formation of a mixture of cyclohexylideneacetic acid (m.p. 90-91°) and a liquid acid, the amide of which had m.p. 186-187° and which failed to give a melting point depression when mixed with the amide of the acid obtained from the liquid portion of the oxidation product from aldehyde B (see above), and which proved to be identical with the amide of hexahydrobenzoic acid.

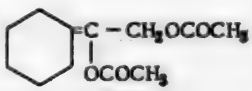
Inasmuch as we had established earlier that hexahydrobenzoic acid is predominantly formed in the oxidation of ω-acetoxyhexahydroacetophenone under these conditions [17], then undoubtedly the 3rd fraction is intermediate and constitutes a mixture of cyclohexylideneacetaldehyde and ω-acetoxyhexahydroacetophenone.

Analysis of the 5th fraction (b.p. 113-114.5° at 3 mm) revealed that it is devoid of carbonyl groups and that it has the empirical formula $C_{12}H_{18}O_4$. Labile hydrogen is absent. Molecular weight 226. Proceeding from these data, it could be assumed that this substance is the dehydration product of 1,1-pentamethyleneglycerol 2,3-diacetate, which under the observed reaction conditions is fully permissible. The fact that the xylene distilled off during the course of the reaction was always slightly cloudy, even though we took complete measures each time to prevent the entrance of moisture into the reaction sphere, can serve as some support for this assumption.

The dehydration of the starting 1,1-pentamethyleneglycerol 2,3-diacetate can proceed in two directions with the formation of the unsaturated diacetates (VI) and (VII):



(VI)

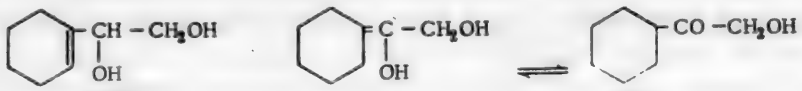


(VII)

Numerous attempts to demonstrate the presence of a double bond in this substance by the method of catalytic hydrogenation proved unsuccessful. However, this fact still does not indicate the absence of a double bond, insofar as it is known that certain unsaturated compounds, in which both of the carbon atoms of the double bond are substituted, under ordinary conditions are hydrogenated with extreme difficulty or not at all [13]. Attempts to brominate the compound also proved unsuccessful. In the bromination reaction the evolution of hydrogen bromide was observed. The obtained product proved to be a liquid that decomposed when distillation was attempted. Analysis of the product revealed it to be a mixture of dibromide and monobromide.

However, saponification of the 5th fraction with alcoholic potassium hydroxide solution gave a crystalline substance with m.p. 52-52.8°. Analysis of this substance revealed that it contains 2 hydroxyl groups and has the empirical formula $C_8H_{14}O_2$. Consequently, saponification resulted in the cleavage of two acetyl groups.

From its structure the obtained diol (m.p. 52-52.8°) should correspond to one of the two structural formulas (VIII) or (IX):



(VIII) (IX)

If the product obtained by saponification had the structure depicted by formula (IX), then it should enter into the reactions characteristic for its ketone form and should give the corresponding phenylhydrazone or osazone. However, we were unable to obtain these derivatives. From this it follows that the given diol is Δ^1-cyclohexenylethylene glycol (VIII).

To confirm the indicated postulation this compound was oxidized with periodic acid. Exactly 1 mole of periodic acid was consumed in the oxidation. From the reaction solution there were isolated formaldehyde, as the dimedon derivative (m.p. 188-189°), and 2,3,4,5-tetrahydrobenzaldehyde, characterized as the semicarbazone (m.p. 212-213°) [14, 15].

Consequently, the diol (m.p. 52-52.8°) has the structure Δ^1-cyclohexenylethylene glycol (VIII), while the substance composing the 5th fraction has the structure of its diacetyl derivative (VI).

EXPERIMENTAL*

Transformation of 1,1-Pentamethyleneglycerol 2,3-Diacetate [2] by Heating with Zinc Dust.

In a four-necked flask, fitted with a brass anchor-type stirrer (cut exactly to fit the bottom of the flask), thermometer and fractionation column, connected to a descending air condenser, was placed 1600 ml of pure dry xylene (b.p. 137-141°). With vigorous stirring into the flask there was introduced 300 g of zinc dust, which had been previously activated by shaking twice with 900 ml of 2% hydrochloric acid, then rapidly washed with water, alcohol, anhydrous alcohol, and dried at 100° under a vacuum of 2-2.5 mm over phosphoric anhydride for 2-3 hours.

The mixture of xylene and zinc dust was heated to the boiling point of xylene and the xylene was partially distilled off to assure an anhydrous medium for the reaction. After cooling the mixture down to 90-100° a solution of 29.75 g of 1,1-pentamethyleneglycerol 2,3-diacetate in anhydrous xylene was introduced into the flask, and the reaction mass was held for 5-6 hours at the boiling point of xylene with constant stirring. For removal from the reaction sphere of the acetic acid formed by cleavage in the reaction a periodic slow distillation was made during the whole course of the reaction to remove a mixture of xylene and acetic acid** through the fractionation column the rate of removal being approximately 20-30 ml every half hour. The amount of acetic acid in the distillate fractions was determined by titration with 0.1 N sodium hydroxide solution.

Time (in hours from the start of the reaction)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Milliliters of 0.1 N NaOH required for titration	0.5	0.5	2.2	9	12	16	12	25	7.1	6

The total amount of titrated acetic acid was approximately 10% of the theoretical based on reacted pentamethyleneglycerol diacetate.

Toward the end of reaction the zinc dust aggregated into lumps, which made stirring difficult. After cooling the reaction mass, the zinc dust was filtered and washed several times on the filter with pure xylene. The combined filtrate was washed with 2% sulfuric acid, water, soda solution, water, and dried over anhydrous sodium sulfate. After removal of the xylene the residue was subjected to fractional distillation in vacuo at 2 mm. The following fractions were obtaned: 1st, b.p. 40-50°, 0.4 g; 2nd, b.p. 78-95°, 1.45 g; 3rd, b.p. 95-100°, 0.7 g; 4th, b.p. 105-110°, 10.83 g; 5th, b.p. 112-116°, 1.4 g; 6th, b.p. 126-135°, 7.67 g.

For further investigation the fractions were redistilled.

1st Fraction, B. p. 48-50° (1.5-2 mm). Aldehyde A.

The quite mobile colorless liquid gives the characteristic intense crimson color with acid fuchsin (Schiff's reagent); forms the silver mirror when reacted in the cold with an ammoniacal silver oxide solution; separates a yellow deposit of cuprous oxide when reacted in the cold with Fehling solution.

* All of the given melting points are corrected.

** The azeotropic mixture of m-xylene and acetic acid, containing 27.5% acetic acid, boils at 115.4°.

The Semicarbazone of Aldehyde A is obtained as glistening colorless plates. After recrystallization from dilute ethyl alcohol, m.p. 156-157°.

4.411 mg substance: 9.601 mg CO_2; 3.651 mg H_2O. 4.628 mg substance: 10.011 mg CO_2; 3.728 mg H_2O. 3.100 mg substance: 0.647 ml N_2 (27°, 734 mm).

	Found %:	C 59.39, 59.03;	H 9.26, 9.01;	N 22.92
$C_9H_{17}ON_3$	Calculated %:	C 58.99;	H 9.35	N 22.93.

Hydrogenation of Cyclohexylideneacetaldehyde Semicarbazone. A solution of 0.1385 g of cyclohexylideneacetaldehyde semicarbazone (see below for preparation) in anhydrous alcohol was hydrogenated in the presence of a skeletal nickel catalyst at room temperature and atmospheric pressure. The hydrogenation was terminated after the absorption of 1.05 moles of hydrogen (20 ml at 20° and 744 mm). The catalyst was filtered from the solution and washed with alcohol. After removal of the solvent there was obtained 0.125 g of cyclohexylacetaldehyde semicarbazone, which after recrystallization from 50% ethanol melted at 157-158°.

From the literature, m.p. 153° [8], 162° [9], 132.5-133.5° [10], 162-163° [11], 157-159° [12].

The semicarbazone of cyclohexylacetaldehyde had the same properties and crystal form under the microscope as the semicarbazone of aldehyde A, and failed to give a melting point depression when mixed with it.

2nd Fraction, B. p. 76-80° (2 mm). Aldehyde B.

A fairly mobile colorless liquid with a characteristic aldehyde odor. Gives the characteristic intense violet color with acid fuchsin (Schiff's reagent); forms the silver mirror when reacted in the cold with ammoniacal silver oxide solution; separates a yellow deposit of cuprous oxide when reacted in the cold with Fehling solution.

The Semicarbazone of Aldehyde B is obtained as fine white crystals. After recrystallization from dilute alcohol, m.p. 208-209° (decompn.).

3.518 mg substance: 7.687 mg CO_2; 2.590 mg H_2O. 3.720 mg substance: 8.079 mg CO_2; 2.760 mg H_2O. 2.810 mg substance: 0.592 ml N_2 (23°, 733 mm).

	Found %:	C 59.63, 59.27;	H 8.23, 8.30;	N 23.45.
$C_9H_{15}ON_3$.	Calculated %:	C 59.64;	H 8.34	N 23.20.

The ultraviolet absorption spectra of aldehyde B and its semicarbazone (in alcohol) are characterized by the following absorption bands:* for the aldehyde λ_{max} 2400 A; for the semicarbazone λ_{max} 2730 A [4,5].

2,4-Dinitrophenylhydrazone of Aldehyde B. To 0.4 g of 2,4-dinitrophenylhydrazine, dissolved in 0.8 ml of warm concentrated sulfuric acid, was added 8 ml of anhydrous ethyl alcohol and an alcohol solution of 0.25 g of the aldehyde. On cooling, the 2,4-dinitrophenylhydrazone precipitated immediately as glistening red plates, which were filtered and washed with alcohol. After recrystallization from a mixture of alcohol and ethyl acetate, m.p. 200-200.5°.

3.093 mg sub.: 0.506 ml N_2 (23°, 733 mm). Found %: N 18.21. $C_{14}H_{18}O_4N_4$. Calculated %: N 18.41.

Thiosemicarbazone of aldehyde B. To 0.5 g of aldehyde B was added a saturated aqueous solution of 0.4 g of thiosemicarbazide. On cooling, the thiosemicarbazone separated as glistening colorless plates. After recrystallization from 65% alcohol, m.p. 166°.

4.350 mg sub.: 5.179 mg $BaSO_4$. 2.787 mg sub.: 0.530 ml N_2 (23°, 739 mm). Found %: S 16.36; N 21.34. $C_9H_{17}N_3S$. Calculated %: S 16.26; N 21.29.

Oxidation of aldehyde B. To a solution of 1.56 g of the aldehyde in 10 ml of alcohol was added 50 ml of water. To the obtained emulsion was added a solution of 5.13 g of silver nitrate in 21 ml of water and then in small portions with stirring a solution of 2.85 g of sodium hydroxide in 24 ml of water was added. After addition of all of the alkali the stirring was continued for another half-hour, until the solution over the precipitate had become completely clear. The precipitate was filtered and washed with hot water. The filtrate and wash waters were extracted with ether to remove neutral impurities, after which the water layer was acidified with dilute hydrochloric acid until acid to Congo and exhaustively extracted with ether. The ether solution was dried over anhydrous sodium sulfate.

After removal of the solvent, there was obtained 0.85 g of acidic substance, which almost completely crystallized as long stout needles. The oxidation product always contained a certain amount of liquid (see below). The

* A "Hilger" quartz spectrograph (middle model) was used to take the absorption spectra. An MF-2 microphotometer was used for the photometric measurements.

crystalline acid was pressed on porous plate and then recrystallized twice from 50% methanol; m.p. 91-92°. The acid is readily soluble in alcohol, chloroform, acetone, benzene, ether and sodium bicarbonate solution; insoluble in water.

3.589 mg sub.: 9.054 mg CO_2; 2.749 mg H_2O. 3.879 mg sub.: 9.722 mg CO_2; 2.960 mg H_2O. 64.0 mg sub.: 4.5 ml 0.1 N NaOH. Found %: C 68.84, 68.25; H 8.57, 8.54. M 142. $C_8H_{12}O_2$. Calculated %: C 68.54; H 8.62. M 140.

Amide of the crystalline acid. A benzene solution of 0.5 g of the obtained acid with m.p. 91-92° was added dropwise to a benzene solution of 2.13 g of thionyl chloride. The mixture was kept at room temperature for 1 hour, after which it was heated at 50-60° for 1 hour. After cooling, the excess thionyl chloride together with benzene was distilled in vacuo at 20-25°

Into a flask with anhydrous benzene was passed dry ammonia and simultaneously a benzene solution of the acid chloride of the acid was added dropwise. The deposited crystals were filtered and washed with water to remove ammonium chloride. From the benzene filtrate after distilling off the benzene there was obtained an additional small amount of the amide. A total of 0.465 g of amide was obtained, which after 2 recrystallizations from hot water had m.p. 146.5-147.5° The amide of the acid was obtained as glistening colorless plates; soluble in alcohol, acetone and chloroform, difficultly soluble in benzene, insoluble in water and ether.

3.346 mg sub.: 8.489 mg CO_2; 2.808 mg H_2O. 3.545 mg sub.: 8.963 mg CO_2; 2.973 mg H_2O. 5.493 mg sub.: 0.552 ml N_2 (24°, 723 mm). 4.800 mg sub.: 0.442 ml N_2 (22°, 730 mm). Found %: C 69.23, 69.00; H 9.39, 9.38; N 9.80, 9.78. $C_8H_{13}ON$. Calculated %: C 69.03; H 9.41; N 10.06.

Amide of the liquid acid. A small amount of liquid acid was extracted from the porous plate, from which the amide was obtained by the method described above. After recrystallization from benzene there were obtained colorless platelike crystals with m.p. 186-187°. The substance is soluble in chloroform, alcohol, and on heating in benzene; insoluble in water, ether and acetone.

Cyclohexlideneacetic acid (IV) was synthesized from cyclohexanone and ethyl bromoacetate through 1-hydroxycyclohexaneacetic acid [7] and had m.p. 91-92°; the amide of this acid melted at 146.5-147.5°. Cyclohexylideneacetic acid and its amide failed to show a melting point depression when mixed with the solid acid obtained from the oxidation of aldehyde B and with its amide.

Cyclohexylideneacetaldehyde (III), which was synthesized from 1-vinyl-1-cyclohexanol through cyclohexylidenethyl alcohol [5], had the same characteristic odor as aldehyde B, and gave an intense violet color with acid fuchsin (Shiff's reagent).

The semicarbazone of cyclohexylideneacetaldehyde melted at 208-209° (decomposition) and failed to show a melting point depression when mixed with the semicarbazone from aldehyde B.

The oxidation of cyclohexylideneacetaldehyde with silver oxide in alkaline medium, under exactly the same conditions as for the oxidation of aldehyde B, gave pure completely crystalline cyclohexylideneacetic acid with m.p. 89-90°. After recrystallization from 50% methanol, m.p. 91-92°.

3rd fraction, b.p. 95-100° (2 mm).

This fraction was a clear colorless liquid and gave a faint violet color with acid fuchsin (Schiff's reagent).

Oxidation of the 3rd fraction. 1.1 g of substance was oxidized with silver oxide in alkaline medium under the conditions described above for the oxidation of aldehyde B. After removal of the solvent there was obtained 0.62 g of acidic substance, which on cooling partially crystallized. The crystals, separated from the liquid phase and recrystallized from aqueous methanol, melted at 91-92° and failed to give a melting point depression when mixed with cyclohexylideneacetic acid.

From 0.5 g of the liquid oxidation product there was obtained 0.42 g of the amide, which after recrystallization from benzene had m.p. 186-187°. A test with potassium permanganate solution revealed that the amide is saturated.

3.816 mg sub.: 9.262 mg CO_2; 3.431 mg H_2O. 4.001 mg sub.: 9.731 mg CO_2; 3.617 mg H_2O. 7.103 mg sub.: 0.696 ml N_2 (21°, 742 mm). Found %: C 66.24, 66.37; H 10.06, 10.11; N 11.11. $C_7H_{13}ON$. Calculated %: C 66.11; H 10.30; N 11.02.

The isolated amide failed to give a melting point depression when mixed with the amide of the acid obtained in very small amount from the oxidation of aldehyde B, and also with the known amide of hexahydrobenzoic acid.

4th fraction, b.p. 105-110° (2 mm).

The fourth fraction was ω-acetoxyhexahydroacetophenone. A fairly mobile colorless liquid, readily soluble in the common organic solvents: alcohol, ether, acetone, benzene, chloroform and ethyl acetate, insoluble in water. After redistillation, b.p. 103-104° (2 mm).

From the literature [3]: b.p. 100-101° (1 mm), n_D^{23} 1.4630, d_4^{23} 1.052, MR_D 48.20; calculated 47.85.

After a short time, the ω-acetoxyhexahydroacetophenone completely crystallized. Long needles, m.p. 42-43°.

4.089 mg sub.: 9.779 mg CO_2; 3.119 mg H_2O. 4.790 mg sub.: 11.485 mg CO_2; 3.619 mg H_2O. 13.699 mg sub.: 0.45 ml CH_4 (21°, 747 mm). 13.720 mg sub.: 0.46 ml CH_4 (21°, 747 mm). Found %: C 65.26, 65.43; H 8.53, 8.45; active H 0.13, 0.14. $C_{10}H_{18}O_3$. Calculated %: C 65.20; H 8.75; active H 0.00.

Semicarbazone of ω-acetoxyhexahydroacetophenone – long thin needles. After recrystallization from 50% ethyl alcohol, m.p. 149-150°.

From the literature [3]: m.p. 149-150°.

2.981 mg sub.: 5.995 mg CO_2; 2.092 mg H_2O. 4.525 mg sub.: 0.699 ml N_2 (20°, 732 mm). Found %: C 54.88; H 7.85; N 17.33. $C_{11}H_{19}O_3N_3$. Calculated %: C 54.75; H 7.94; N 17.40.

2,4-Dinitrophenylhydrazone of ω-acetoxyhexahydroacetophenone. Acetoxyhexahydroacetophenone (0.2 g) was dissolved in glacial acetic acid and to the solution was added 0.216 g of 2,4-dinitrophenylhydrazine. The mixture was heated and then allowed to stand for 12 hours at room temperature. After distilling off the acetic acid in vacuo there were obtained fine yellow crystals, which after 2 recrystallizations from alcohol had m.p. 130.5-131°.

2.770 mg sub.: 0.379 ml N_2 (21.5°, 730 mm). Found %: N 15.22. $C_{16}H_{20}O_8N_4$. Calculated %: N 15.38.

ω-Hydroxyhexahydroacetophenone. To 2.37 g of ω-acetoxyhexahydroacetophenone was added an alcohol solution of 1.35 g of potassium hydroxide, and the mixture stood for 12-14 hours at room temperature. Then the alcohol was distilled off, the reaction mass poured into water, and extracted with ethyl acetate. After removal of the solvent there was obtained 1.06 g of ω-hydroxyhexahydroacetophenone with b.p. 95-97° at 4 mm.

From the literature [16]: b.p. 95° (4 mm).

2,4-Dinitrophenylosazone of ω-hydroxyhexahydroacetophenone. 2,4-Dinitrophenylhydrazine (1.63 g) was dissolved in 3 ml of warm concentrated sulfuric acid. To the obtained solution were added 20 ml of anhydrous ethyl alcohol and an alcohol solution of 0.53 g of ω-hydroxyhexahydroacetophenone, and the mixture was brought up to the boil. Yellowish red crystals were obtained on cooling, which were washed with alcohol. The substance is insoluble in both the ordinary organic solvents and in water. After recrystallization from nitrobenzene the 2,4-dinitrophenylosazone had m.p. 259-260° (decomposition).

2.994 mg sub.: 5.279 mg CO_2; 1.111 mg H_2O. 3.401 mg sub.: 6.009 mg CO_2; 1.269 mg H_2O. 3.743 mg sub.: 0.743 ml N_2 (22°, 726 mm). Found %: C 48.11, 48.22; H 4.15, 4.18; N 21.93. $C_{20}H_{20}O_8N_8$. Calculated %: C 47.99; H 4.03; N 22.39.

5th fraction, b.p. 112-116° (2 mm). The mobile colorless and odorless liquid is readily soluble in the ordinary organic solvents and insoluble in water.

B.p. 113-114.5° (3 mm), $n_D^{19.5}$ 1.4692, $d_4^{19.5}$ 1.076, MR_D 58.58; calculated 58.26.

4.740 mg sub.: 11.030 mg CO_2; 3.375 mg H_2O. 4.101 mg sub.: 9.603 mg CO_2; 2.940 mg H_2O. 16.53 mg sub.: 0.36 ml CH_4 (19°, 747 mm). 10.80 mg sub.: 103.3 mg camphor: Δt 18.7°. Found %: C 63.50, 63.90; H 7.97, 8.02; active H 0.088. M 224. $C_{12}H_{18}O_4$. Calculated %: C 63.70; H 8.02; active H 0.00. M 226.

Bromination of the 5th fraction. To a solution of 0.45 g of the substance in carbon tetrachloride was cautiously added with cooling a solution of 0.102 ml of bromine in carbon tetrachloride. Decolorization proceeded slowly and some evolution of hydrogen bromide was observed. After distilling off the solvent we found that the product could not be distilled without decomposition.

7.579 mg sub.: 5.982 mg AgBr. Found %: Br 33.59. $C_{12}H_{17}O_4Br$. Calculated %: Br 26.19. $C_{12}H_{18}O_4Br_2$. Calculated %: Br 41.40.

Saponification of the 5th fraction. To an alcohol solution of 1.18 g of the substance was added an alcohol solution of 0.7 g of potassium hydroxide. After 12-14 hours, the mixture turned yellow. At first the odor of ethyl

acetate was detected, which soon vanished. The alcohol from the reaction mixture was distilled in vacuo at room temperature, and water was added to the residue. The obtained solution was filtered and thoroughly extracted with ethyl acetate. After drying over anhydrous sodium sulfate and distilling off the solvent there remained 0.567 g of an oil, which completely crystallized on cooling; m.p. 44-49°. After recrystallization from petroleum ether (b.p. 50-70°) the substance was obtained as very fine long needles, m.p. 52-52.8°.

The obtained substance is extremely soluble in the ordinary organic solvents and in water, insoluble in the cold in petroleum ether.

3.246 mg sub.: 8.045 mg CO_2; 2.989 mg H_2O. 4.151 mg sub.: 10.254 mg CO_2; 3.639 mg H_2O. 6.275 mg sub.: 2.06 ml CH_4 (19°, 763 mm). 5.801 mg sub.: 1.90 ml CH_4 (19°, 763 mm). Found %: C 67.64, 67.41; H 10.30, 9.81; active H 1.38. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.93; active H 1.4.

A precipitate of neither the hydrazone nor the osazone is obtained when this substance is reacted with 2,4-dinitrophenylhydrazine in the usual manner.

Periodic acid oxidation of the substance with m.p. 52-52.8°. Two experiments were performed; a) to determine the consumption of periodic acid, and b) to isolate the oxidation products.

a) To 0.0284 g of the substance, dissolved in a small amount of water, was added 5 ml of periodic acid solution containing 0.05056 g of HIO_4. After 1.5 hours, to the solution was added 150 mg of sodium bicarbonate, 5 ml of 0.05 N sodium arsenite solution, and 0.4 ml of a 20% potassium iodide solution. After 10 minutes, the excess arsenite was back titrated with 0.05 N iodine solution.

2.8 ml of 0.05 N iodine solution was used for the back titration, which is equivalent to 0.0107 g of HIO_4; consequently, the amount of reacted periodic acid was 0.0399 g. The theoretical amount of periodic acid required for the oxidation of two adjacent hydroxyl groups is 0.0384 g.

b) To 0.0853 g of the substance with m.p. 52-52.8° in a small amount of water was added 12 ml of periodic acid solution containing 0.1213 g of HIO_4. A characteristic odor, reminiscent of the odor of benzaldehyde, immediately appeared. The mixture was kept at room temperature for 1.5 hours, after which it was exhaustively extracted with ether. The ether solution was washed with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, the ether was distilled off and to the residue, dissolved in a small amount of alcohol, was added a 50% alcohol solution of semicarbazide. After some time, the semicarbazone of 2,3,4,5-tetrahydrobenzaldehyde separated as fine white crystals, insoluble in ether, acetone, benzene and water, soluble in alcohol. Yield 59 mg. After recrystallization from dilute ethyl alcohol, m.p.212-213°.

From the literature [14, 15]: m.p. 211-212°, 212-213°.

3.192 mg sub.: 6.737 mg CO_2; 2.294 mg H_2O. 4.087 mg sub.: 8.633 mg CO_2; 2.890 mg H_2O. 3.050 mg sub.: 0.689 ml N_2 (25°, 731 mm). Found %: C 57.59, 57.64; H 8.04, 7.91; N 24.90. $C_8H_{13}ON_3$. Calculated %: C 57.46; H 7.84; N 25.13.

The aqueous layer, remaining after ether extraction of the 2,3,4,5-tetrahydrobenzaldehyde, was treated with saturated dimedon solution. After prolonged standing there was obtained 0.1644 g of a voluminous white precipitate, which after recrystallization from alcohol had m.p. 188-189°, and which failed to show a melting point depression when mixed with authentic formyl dimedon.

6th fraction, b.p. 126-135° (2 mm).

This fraction was a viscous colorless oil, essentially composed of original 1,1-pentamethyleneglycerol 2,3-diacetate. After redistillation, b.p. 127-129° (2 mm).

5.206 mg sub.: 11.338 mg CO_2 3.851 mg H_2O. 16.501 mg sub.: 1.65 ml CH_4 (22°, 735 mm). Found %: C 59.43; H 8.28; active H 0.40. $C_{12}H_{20}O_5$. Calculated %: C 59.00; H 8.25; active H 0.41.

SUMMARY

1. The transformation of 1,1-pentamethyleneglycerol 2,3-diacetate into ω-acetoxyhexahydroacetophenone under the conditions of the Serini reaction was studied.

2. The secondary products obtained in this reaction were isolated, characterized, and identified: cyclohexylacetaldehyde, cyclohexylideneacetaldehyde and the diacetate of Δ^1-cyclohexenylethylene glycol.

3. The structure of cyclohexylacetaldehyde and of cyclohexylideneacetaldehyde was confirmed by known syntheses. The structure of the diacetate of Δ^1-cyclohexenylethylene glycol was proved by the method of identifying the products obtained in the oxidative cleavage of Δ^1-cyclohexenylethylene glycol with periodic acid.

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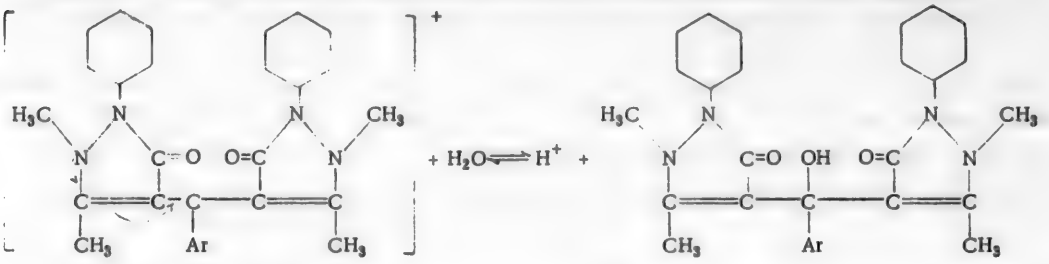
* See Consultants Bureau Translation, page 323, this issue.

DYES CONTAINING ANTIPYRINE NUCLEI

IV. ACID AND BASIC PROPERTIES OF DYES

O. F. Ginzburg, D. V. Ioffe and N. S. Melnikova

A previous communication showed [1] that dyes containing antipyrine nuclei undergo hydrolysis in aqueous solutions as do other triarylmethane dyes, and that it proceeds in accordance with the equation:



To clarify the influence of various aromatic radicals (Ar) on the acid-base properties or antipyrine dyes and the carbinol compounds formed therefrom, the hydrolysis compounds of previously-synthesized antipyrine dyes were determined [2], and also of those newly obtained by oxidation, diantipyryl-m-methoxyphenylmethane, diantipyryl-3,4-dimethoxyphenylmethane and diantipyryl-m-nitrophenylmethane. The hydrolysis constants of these dyes were calculated in accordance with equation (1) on the basis of experimental data obtained by measuring the optical density, E, and the pH values of aqueous solutions of the dyes, after equilibrium had been attained in the given solutions.

$$K_h = \frac{E_{max} - E}{E}[H^+]. \qquad (1)$$

E_{max}, the optical density of a solution of the dye in which hydrolysis is almost completely suppressed, is determined by computation from equation (2)

$$E_{max} = \frac{E_1 E_2 (1-n)}{E_2 - nE_1}, \qquad (2)$$

where

$$n = \frac{[H_2^+]}{[H_1^+]},$$

or by employing the method of least squares for the computation of experimental data.

TABLE 1

No.	Ar	K_h
1	p-$(CH_3)_2NC_6H_4$	$1.38 \cdot 10^{-11}$
2	m, p-$(CH_3O)_2C_6H_3$	$1.24 \cdot 10^{-8}$
3	α-$C_{10}H_7$	$2.14 \cdot 10^{-8}$
4	m-$CH_3OC_6H_4$	$1.78 \cdot 10^{-7}$
5	C_6H_5	$2.50 \cdot 10^{-7}$
6	m-$O_2NC_6H_4$	$9.70 \cdot 10^{-6}$
7	p-$O_2NC_6H_4$	$1.77 \cdot 10^{-5}$

Table 1 presents the values determined for the hydrolysis constants of antipyrine dyes (1) at 17 ± 1°.

It should be noted that the values of dye hydrolysis constants (5) and (7) in Table 1, correspond quite satisfactorily to the values of those constants computed earlier on the basis of experimental data obtained by potentiometric titration of dye solutions [1].

Examination of the table shows that the character of the aromatic radical strongly affects the hydrolysis constants of antipyrine dyes and, consequently, the basicity constants of the carbinol compounds derived from the dyes; and in this connection, the effect of the dimethylamino, methoxy and nitro groups in the para and meta positions relative to the central carbon atom of the benzene ring, upon the basicity of carbinol compounds is analogous to the effect of these groups upon the basicity of amines in the benzene series. At the same time, the dissociation constant of diantipyryl-α-naphthylcarbinol is greater than that of diantipyryl-phenylcarbinol, despite the fact that α-naphthylamine is known to be a less basic compound than aniline.

EXPERIMENTAL

Diantipyryl-m-methoxyphenylmethane

Base. 30 ml hydrochloric acid (d 1.17) was added to a solution of 15 g antipyrine (0.06 mole) and 5.45 g (0.04 mole) m-methoxybenzaldehyde in 90 ml alcohol. The next day the white precipitate that came down was filtered out and the alcohol driven off the filtrate. After the alcohol was driven off, a new batch of the hydrochloride came down, which was filtered out and added to the first batch. The base was obtained by treating the hydrochloride with a dilute sodium carbonate solution. This gave 17.0 g (86%) base, m.p. 170°. After two crystallizations from a benzene-gasoline mixture (1:1), m.p. was 186°. Further crystallization led to no further rise in temperature.

0.1103 g sub.: 11.0 ml N_2 (23°, 780 mm). Found %: N 11.62. $C_{30}H_{30}O_3N_4$. Calculated %: N 11.33.

The hydrochloride crystallized from water. It was dried in a desiccator over sulfuric acid. Melted at 141-142° (with decomposition). The presence of hydrogen chloride in the salt was established in all experiments by potentiometric titration with an aqueous acetone solution.

0.2630 g sub.: 10.25 ml 0.1 N NaOH (T 0.00371). Found %: HCl 13.19. $C_{30}H_{30}O_3N_4 \cdot 2HCl$. Calculated %: HCl 12.89.

The picrate of the base crystallized from alcohol, m.p. 195°.

0.1177 g sub.: 13.8 ml N_2 (23°, 778 mm). Found %: N 13.71. $C_{30}H_{30}O_3N_4 \cdot C_6H_3O_7N_3$. Calculated %: N 13.55.

TABLE 2

No.	Compound	M.p.	Dye solution (ml)	λ mμ	E_{max}	pH	E	pK_a
1	Diantipyryl-p-dimethylaminophenylcarbinol	135-136°	0.10	550	0.368	9.75 10.85	0.342 0.183	3.30 3.32
2	Diantipyryl-3,4-dimethoxyphenylcarbinol picrate	118-120	0.60	500	0.456	6.99 7.25	0.406 0.374	6.27 6.26
3	Diantipyryl-α-naphthylcarbinol	235-236	0.60	470	1.192	7.36 7.84	0.792 0.483	6.51 6.50
4	Diantipyryl-m-methoxyphenylcarbinol picrate	148-151	0.60	490	0.482	6.40 6.99 7.25	0.334 0.170 0.115	7.42 7.43 7.43
5	Diantipyrylphenylcarbinol	172-173	0.80	480	1.082	5.90 6.34	0.905 0.701	7.57 7.56
6	Diantipyryl-m-nitrophenylcarbinol picrate	111-113	0.60	480	0.633	4.01 4.43 5.05	0.576 0.497 0.304	9.16 9.17 9.16
7	Diantipyryl-p-nitrophenylcarbinol	180-181	0.60	500	1.117	4.01 4.43 5.05	0.928 0.775 0.398	9.47 9.40 9.44

Diantipyryl-3,4-dimethoxyphenylmethane

Base. Obtained in the same manner as for diantipyryl-m-methoxyphenylmethane; yield 95%. M.p. 200° after crystallization from benzene-gasoline mixture (1:1).

0.1082 g sub.: 9.8 ml N_2 (22°, 770 ml). Found %: N 10.52. $C_{31}H_{32}O_4N_4$. Calculated %: N 10.56.

Hydrochloride. Crystallized from water. Dried in desiccator over sulfuric acid. Melted at 176-177° with decomposition.

0.3077 g sub.: 11.20 ml 0.1 N NaOH (T 0.00371). Found %: HCl 12.30. $C_{31}H_{32}O_4N_4 \cdot 2HCl$. Calculated %: HCl 12.24.

Picrate of base, m.p. 160°, from alcohol.

0.0946 g sub.: 10.6 ml N_2 (22°, 770 mm). Found %: N 13.01. $C_{31}H_{32}O_4N_4 \cdot C_6H_3O_7N_3$. Calculated %: N 13.01.

Diantipyryl-m-nitrophenylcarbinol picrate

5 g diantipyryl-m-nitrophenylmethane was dissolved upon heating in 50 ml concentrated hydrochloric acid. 0.3 g sodium nitrite was added, bit by bit, to the hot solution within 3 or 4 minutes, and 1.4 ml nitric acid (d 1.4) was then added dropwise in 20 minutes. Next day the orange-colored solution was filtered, and a 15% sodium hydroxide solution added until a precipitate came down. 2% sodium hydroxide solution was then added slowly, by drops, in 2 hours, until phenolphthalein showed an alkaline reaction. The next day, the solution with its precipitate was heated to boiling. After cooling, the precipitate was filtered and dried. 1.85 g of the base was obtained. 0.85 g picric acid in 20 ml alcohol was added to a solution of the base in 50 ml alcohol. The precipitate deposited was filtered out the next day. The precipitate was crystallized from alcohol, m.p. 148-151°. λ_{max} of the dye cation was 490 mμ.

0.1191 g sub.: 15.7 ml N_2 (16°, 757 mm). 0.1126 g sub.: 14.8 ml (16°, 757 mm). Found %: N 15.44, 15.45. $C_{29}H_{26}O_4N_5 \cdot C_6H_2O_7N_3$. Calculated %: N 15.21.

Diantipyryl-m-methoxyphenylcarbinol picrate

Obtained in the same manner as diantipyryl-m-nitrophenylcarbinol picrate. Crystallized from 50% alcohol. M.p. 111-113°. λ_{max} of the dye cation was 490 mμ.

0.1510 g sub.: 17.6 ml N_2 (22°, 776 mm). 0.1015 g sub.: 12.4 ml N_2 (24°, 752 mm). Found %: N 13.63, 13.74. $C_{30}H_{23}O_3N_4 \cdot C_6H_2O_7N_3$. Calculated %: N 13.59.

Diantipyryl-3,4-dimethoxyphenylcarbinol picrate.

Obtained in the same manner as diantipyryl-m-nitrophenylcarbinol picrate. Crystallized from 50% aqueous alcohol. M.p. 118-120°. λ_{max} of the dye cation was 500 mμ.

0.1091 g sub.: 12.4 ml N_2 (22°, 776 mm). 0.0778 g sub.: 9.0 ml N_2 (22°, 750 mm). Found %: N 13.30, 13.09. $C_{31}H_{31}O_4N_4 \cdot C_6H_2O_7N_3$. Calculated %: N 13.04.

Dye Hydrolysis Study

$5 \cdot 10^{-5}$ mole of the carbinol compound or picrate of a dye was dissolved in 50 ml acetone. Identical amounts of the acetone solution were added to various buffer solutions of differing pH. After the establishment of equilibrium in the solution, measurement of its optical density was made with a Koenig-Martens spectrophotometer at the wavelength indicated in the table. The layer of solution under study was 20 mm thick, the temperature 17 ± 1°. The data obtained are adduced in Table 2. The same table presents the pK_a values for carbinol compounds obtained from these dyes.

SUMMARY

1. Depending upon the nature of the aromatic radical linked to the central carbon atom in antipyrine dyes, the hydrolysis constants of the latter may differ from each other by more than 10^6 times.

2. Oxidation of diantipyryl-m-methoxyphenylmethane and diantipyryl-3,4-dimethoxyphenylmethane results in the formation of new dyes of the diantipyrylarylmethane series.

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* See Consultants Bureau Translation, page 1761.

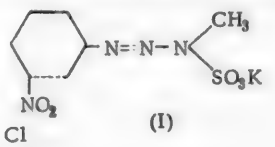
REACTION OF DIAZO COMPOUNDS WITH SULFAMIC ACID AND ITS DERIVATIVES

III. STUDY OF THE HYDROLYTIC DECOMPOSITION REACTIONS OF 1-ARYL-3-METHYLTRIAZENE-3-SULFONIC ACIDS

D. Z. Zavelsky and L. A. Lishnevskaya

In our previous communications, devoted to a study of the reaction of diazo compounds with salts of N-methylsulfamic acid [1] and the properties of the 1-aryl-3-methyltriazene-3-sulfonates obtained in this manner [2], it was mentioned that in the recrystallization of some of the members in this series of compounds from water, or on their dry storage in the air, or on their coming in contact with acids, the removal of sulfonic groups from them by cleavage was observed. As a rule, this cleavage was accompanied by the evolution of nitrogen and a profound change in the nature of the residual molecule.

A more detailed study revealed that the capacity of 1-aryl-3-methyltriazene-3-sulfonates for hydrolytic cleavage of the sulfonic group becomes more strongly developed the greater the electron attraction effect possessed by the aryl containing substituents. In the order of increasing lability of the sulfonic group the investigated triazene-N-sulfonates can be arranged in the following manner: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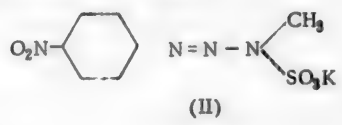
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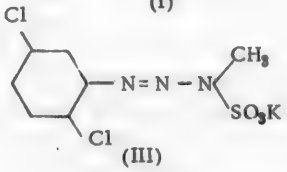
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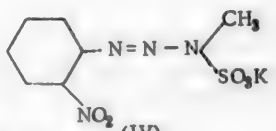
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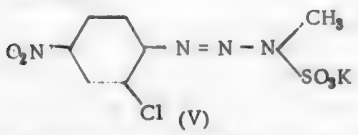
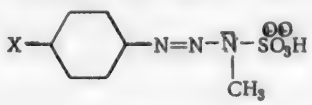
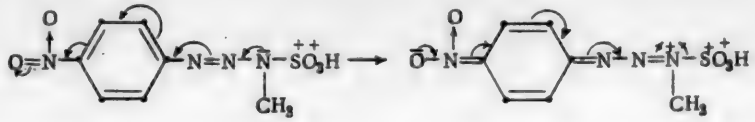

(V)

The reaction rate for the hydrolytic cleavage of the sulfonic group increases with increase in temperatures and with decrease in the pH of the solution.

The observed rule is also in complete accord with the electron theory. An examination of the structure of the arylmethyltriazene-N-sulfonic acid molecule leads to the conclusion that, in order to realize the rupture of the electropositive sulfonic group, it is necessary for the nitrogen, attached to the positively charged sulfur of the sulfonic group, to show a lower electron density under the influence of substituent X.

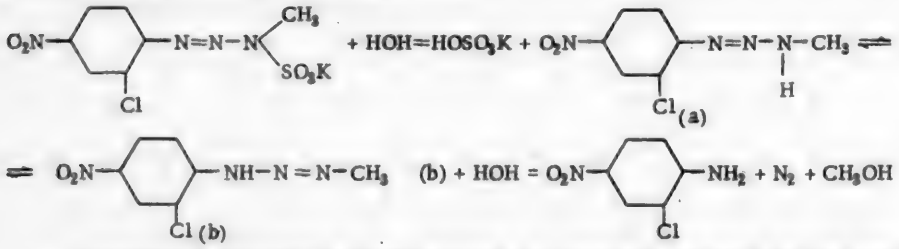


Such an effect can be attained when substituent X possesses electron attraction properties. For example, if X is an electrophilic NO_2 group, the electron displacement will apparently proceed in the following manner:



Naturally, the smaller the electron charge becomes on the terminal nitrogen, the easier the rupture of the bond between it and the positively charged sulfur of the sulfonic group will be; here a role will be played not only by the nature of substituent X, but also by its location, and also by the character and location of the other substituents. Consequently, the m-NO_2 group will weaken the bond between nitrogen and the sulfonic group more than will the m-Cl group, the p-NO_2 group more than the m-NO_2 group, and the o-NO_2 group more than the p-NO_2 group. The presence in the benzene ring, in addition to the p-NO_2 group, of the o-Cl group possessing a negative inductive effect and a positive, but smaller, bonding effect, leads to further weakening of the bond between the nitrogen and sulfur atoms. As can be seen from the above presented series of triazene-N-sulfonates, the total effect of two Cl groups, found in the 2,5-positions, reduces the stability of the bond between nitrogen and the sulfonic group more than does the influence of a NO_2 group in the m- and even in the p-position. It should be mentioned that the bond between nitrogen and the sulfonic group in triazenesulfonates when the NO_2 group is shifted from the m- to the p-position is weakened to a much less degree than when the same group is shifted from the p- to the o-position. On the matter of lability, the bond between nitrogen and the sulfonic group in the triazenesulfonate from o-nitrodiazobenzene stands much closer to the triazenesulfonate from 4-nitro-2-chlorodiazobenzene than to the triazenesulfonates from m-nitrodiazobenzene and p-nitrodiazobenzene.

On boiling aqueous solutions of the triazenesulfonates from 2-nitro- and 4-nitro-2-chlorodiazobenzenes the decomposition proceeds with the formation of the sulfate ion, nitrogen, methyl alcohol and the amines, corresponding to the original diazo compounds, namely 2-nitroaniline and 4-nitro-2-chloroaniline. A detailed study of this process, especially for the example of the triazenesulfonate from 4-nitro-2-chlorodiazobenzene, gives a basis to postulate the following scheme:



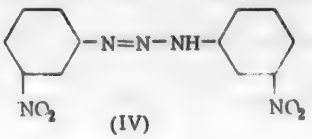
According to this scheme, the first reaction is cleavage of potassium bisulfate and the formation of 4-nitro-2-chlorophenyldiazoaminomethane (a), which tautomerizes into 4-nitro-2-chloroanilinodiazomethane (b). The latter, being extremely labile in acid medium ($KHSO_4$), quickly decomposes, adding water, into 4-nitro-2-chloroaniline, nitrogen and methyl alcohol. As a result of this, the equilibrium of the tautomeric transformation of product (a) into product (b) shifts to the right and the reaction goes to completion.

The proposed scheme is supported by the work of Dimroth [3], who first synthesized the first member of the alkylaryl series of disubstituted triazenes, methylphenyltriazene, and showed that the latter is unstable, not only with respect to strong acids but also toward such a weak acid as carbonic acid. According to Dimroth, methylphenyltriazene under the influence of hydrochloric acid decomposes into aniline, nitrogen and methyl chloride:

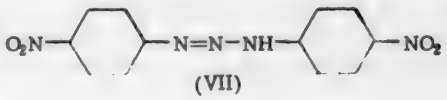
This decomposition reaction is analogous to the one observed by us, with the difference that instead of methyl chloride we obtained methyl alcohol under our reaction conditions. The attempts made by us after cleavage of the sulfonic group to isolate the intermediately formed arylmethyltriazenes proved unsuccessful inasmuch as the presence of the acid bisulfate ion immediately led to the decomposition of the intermediate into arylamine, nitrogen and methyl alcohol.

In contrast to the triazenesulfonates from 4-nitro-2-chlorodiazobenzene and 2-nitrodiazobenzene, the triazenesulfonates from 3-nitro-, 4-nitro- and 2,5-dichlorodiazobenzenes form, when their solutions are boiled in acetate buffer at pH 4.0, besides sulfuric acid, nitrogen and methyl alcohol, not the arylamines

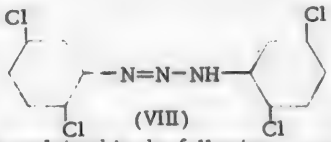
but instead the symmetrical triazenes: 3,3'-dinitrodiphenyltriazene (VI), 4,4'-dinitrodiphenyltriazene (VII) and 2,5,2',5'-tetrachlorodiphenyltriazene (VIII):



(IV)

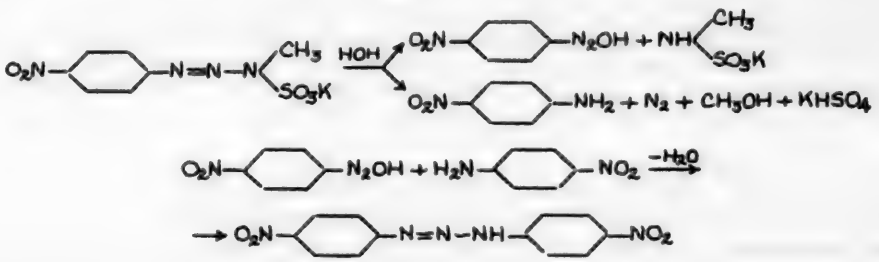


(VII)



(VIII)

This phenomenon can be satisfactorily explained in the following manner. Earlier [4] it had been shown that the less electrophilic the substituents in the benzene ring of methylaryltriazene-N-sulfonates, the easier is the cleavage of the latter in acid medium into diazo compound and methylsulfamic acid, and the more difficult is the cleavage of the bisulfate ion with formation of the aromatic amine. From this it can be concluded that when the substituents in methylaryltriazene-N-sulfonates are the nitro group in positions 3 or 4, or chlorine in the 2,5-positions, the reactions for the formation of the amines proceed at a rate that is equal to or less than the rate for the formation of the diazo compounds, as a result of which in the final end the products formed are not arylamines, but symmetrical diaryltriazenes:

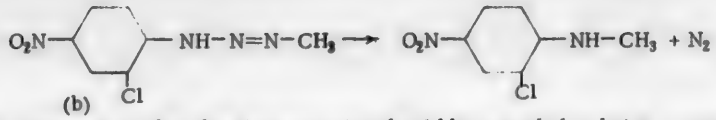


If the substituents in the phenyl nucleus of methylaryltriazene-N-sulfonates possess a more electrophilic character, as, for example, the nitro group in position 2 or, simultaneously, the nitro group in position 4 and chlorine in position 2, the cleavage into diazo compound and methylsulfamic acid proceeds at a considerably slower rate than does the cleavage into bisulfate and arylamine, and the final reaction product obtained is essentially the arylamine. A more exact quantitative characterization of the influence of the nature, position and number of substituents in the phenyl nucleus of methylaryltriazene-N-sulfonates can be obtained on the basis of studying the kinetics of both reactions.

A more detailed study of the process for the hydrolysis of the triazenesulfonate from 4-nitro-2-chlorodiazobenzene enabled us to isolate an arylamine, which was identified as 4-nitro-2-chloroaniline by its diazotization and coupling with β-naphthol and ASG acid. However, this amine, even after several recrystallizations, had m.p. 98-99° instead of 107°, the m.p. of authentic 4-nitro-2-chloroaniline, which testified to the presence of a difficultly removable impurity.

Further, it was found that in the diazotization in 15-20% hydrochloric acid of the amine, obtained from the hydrolysis of 1-(4'-nitro-2'chloro)phenyl-3-methyltriazene-3-sulfonate, a precipitate was obtained in the ice-cooled diazo solution, after recrystallization having m.p. 95° and identified by the Liebermann reaction as being a nitrosoamine. A study of the properties of this nitrosoamine revealed it to be 4-nitro-2-chloro-N-nitroso-N-methylaniline. Its structure was indubitably established by the special synthesis of 4-nitro-2-chloro-N-methylaniline and its nitroso derivative, and the identification of these products with the studied nitrosoamine and its hydrolysis product with concentrated hydrochloric acid.

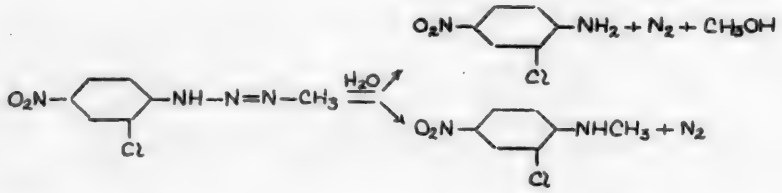
As a result, it was established that in the hydrolytic decomposition of the triazenesulfonate from 4-nitro-2-chlorodiazobenzene there is formed not only 4-nitro-2-chloroaniline, but also its N-methyl derivative. Consequently, together with the principal direction of the decomposition reaction for the arylmethyltriazene, intermediately formed after cleavage of the sulfonic group, it is also possible to have the secondary reaction:



(b)

It appears to us that the given reaction should be regarded as being a methylation of the 4-nitro-2-chloroaniline radical by the daizomethane radical, in which connection it can be assumed that this reaction proceeds intermolecularly more rapidly than it does intramolecularly. From this it also follows that in acid media, the arylalkyltriazenes are in effect inclined to tautomerism from form (a) into form (b).

From an examination of both of the directions for the decomposition of 4-nitro-2-chlorophenylmethyltriazene it can be assumed that the presence of water should favor one of these directions, but not the other:



The verification of this postulation completely confirmed its validity. When 1-(4'-nitro-2'-chloro)-phenyl-3-methyltriazene-3-sulfonate was hydrolyzed in the presence of water we obtained 4-nitro-2-chloro-N-methylaniline in a yield of 6.6% of theory, while when the triazenesulfonate was decomposed as the result of storage, i.e., under the influence of only the moisture found in the air, the yield was 35.5 - 37.0%, i.e. 5-6 times greater.

EXPERIMENTAL

1. Capacity of Arylmethyltriazene-N-sulfonic Acids for Hydrolytic Cleavage of the Sulfonic Group as a Function of Their Structure

The triazene-N-sulfonates, obtained by the diazoamino condensation of potassium methylsulfamate with the diazo compounds from 3-nitroaniline, 4-nitroaniline and 2,5-dichloroaniline, when dissolved in aqueous buffer solutions with pH from 5.0 to 1.0 at room temperature, fail to show any indications of cleavage of the sulfonic group even after 30 minutes.

At 50°-55° for the triazenes from 3-nitroaniline and 4-nitroaniline a buffer with pH 3.0 is already sufficient for the appearance within 5 minutes of traces of sulfate ion, revealed by testing with barium chloride. For the triazenesulfonate from 2,5-dichloroaniline the same result is obtained at 50-55° even in a buffer solution with pH 3.5-4.0; consequently, this triazene cleaves the sulfonic group more readily than do the first two. The triazene-N-sulfonates from 2-nitroaniline and 4-nitro-2-chloroaniline cleave the sulfonic group even more readily. Even their neutral aqueous solutions on heating at the boil for several minutes are capable of showing an acid reaction, caused by cleavage of the bisulfate ion. The appearance of an acid reaction sharply accelerates the hydrolysis process, rapidly driving it to completion.

The triazene-N-sulfonates from 4-nitroaniline and, especially, from 3-nitroaniline, after recrystallization from water, can safely be dried in an oven at 50-70°, and after drying can be stored for months without any indications of decomposition. The moist crystals of the triazenesulfonate from 2,5-dichloroaniline already require drying at a lower temperature, while the dry crystals begin to decompose after 2-6 weeks of storage.

Prior to drying, the moist crystals of the triazene-N-sulfonates from 2-nitroaniline and 4-nitro-2-chloroaniline have to be well pressed on porous clay plate, and then dried either in a vacuum desiccator at room temperature over solid potassium hydroxide, or, more quickly, in an oven at 70° with frequent stirring and disintegration of the crystal lumps. In the recrystallization of these triazene-N-sulfonates from water it is expedient to first make them into a paste with a small amount of cold water, then to add water that has been heated to 70-90° and also made slightly ammoniacal, and after rapid solution with stirring, followed by filtration, to cool immediately for the initiation of crystallization. The addition of ammonia to the water during recrystallization noticeably protects the triazene-N-sulfonates from decomposition also during drying and storage. Even better stabilization is obtained by the addition of either sodium or potassium acetate to the water. It is very difficult to dry the triazenesulfonates from 2- nitroaniline and especially from 4-nitro-2-chloroaniline, not stabilized in this manner, from the mother

liquor without incurring decomposition; when stored in the dry form they decompose within 1 - 4 days.

2. Study of the Decomposition of Triazene-N-Sulfonates During Hydrolytic Cleavage of the Sulfonic Group

a) 1-(4'-Nitro)phenyl-3-methyltriazene-3-sulfonate (II). The triazenesulfonate (2 g) was charged into a flask with 20 ml of pH 4.0 acetate buffer solution and heated for 4 hours at 60-70°, during which time constant foaming of the solution was observed due to the evolution of nitrogen. During the whole time test samples of the solution gave a positive reaction with ASG acid for active diazo compound. Gradually a yellowish-brown precipitate began to separate from the solution.

On conclusion of heating the precipitate was filtered, washed with hot water and dried, the weight was 0.36 g. The obtained substance is insoluble in water and moderately soluble in alcohol, benzene and acetone. After two recrystallizations from benzene the m.p. is 228-230°, under the microscope the crystals appear as yellow leaflets. On heating a sample of the recrystallized product in a solution of glacial acetic acid, containing a small amount of α-naphthylamine, an intense dark cherry red color is obtained, characteristic for diaryltriazenes insoluble in water. On dissolving several crystals of the product in alcohol and adding several drops of sodium hydroxide solution there is obtained a very intense reddish violet coloration. On heating the investigated crystals in dilute aqueous sodium hydroxide solution up to the boil the solution becomes brightly colored, and on cooling is decolorized, depositing bluish violet needles, possessing a greenish bronze cast in reflected light. The described reactions are characteristic for 4,4'-dinitrodiazoaminobenzene [5]. A comparison of the obtained product with authentic 4,4'-dinitrodiazoaminobenzene, synthesized in the conventional manner, by the melting points of the individual products and their mixture demonstrated their complete identity.

The filtrate, obtained on boiling the triazene-N-sulfonate, deposits the unchanged product on cooling. This product is filtered and to part of the mother liquor is added hydrochloric acid and barium chloride, giving a precipitate of barium sulfate.

The main portion of the mother liquor is made alkaline, so as to neutralize the acetic acid present in the acetate buffer solution, and is then distilled. The pale yellow distillate contains methyl alcohol, the presence of which is demonstrated by oxidation of a sample of the distillate with potassium permanganate in 20% sulfuric acid to yield formaldehyde and the color reaction of the latter with phenylhydrazine in the presence of ferric chloride [6].

b) 1-(2',5'-Dichloro)phenyl-3-methyltriazene-3-sulfonate (III) and 1-(3'-nitro)phenyl-3-methyltriazene-3-sulfonate (I). On heating the solutions of these two triazenes in acetate buffer at pH 4.0 under the above described conditions there also occurs cleavage of the sulfonic group, accompanied by the evolution of nitrogen and methyl alcohol and the formation of symmetrical diaryltriazenes, namely, 2,5,2',5'-tetrachlorodiphenyltriazene (VIII) and 3,3'-dinitrodiphenyltriazene (VI).

The cleavage of the sulfonic group proceeds more rapidly for the triazenesulfonate obtained from 2,5-dichlorodiazobenzene (III).

c) 1-(2'-Nitro)phenyl-3-methyltriazene-3-sulfonate (IV). For this triazene the cleavage of the sulfonic group proceeds even on simple boiling of its neutral solution in distilled water. After recrystallization from water without the addition of ammonia and on being allowed to dry overnight in a vacuum desiccator over caustic at room temperature, the precipitate of this triazenesulfonate frequently shows a partial darkening the next morning. When touched with a spatula the discolored portions of the precipitate begin to swell, similar to boiling, and quickly, within a matter of seconds, they encompass all of the new portions of still unchanged crystals and convert them into tar. At the same time nitrogen is evolved. The tarry viscid substance obtained in the decomposition shows a positive reaction for mineral acid when tested with water-moistened Congo paper. The addition of barium chloride to its aqueous extract gives a precipitate of barium sufate. A sample of the tarry substance liquefies when heated in water with the evolution of nitrogen and colors the water an orange yellow. The obtained solution fails to couple with ASG acid, either in neutral medium or after acidification, and consequently contains neither an active nor a passive soluble diazo compound. On adding hydrochloric acid to the investigated solution and then several drops of nitrite the solution becomes colorless and couples with a soda solution of ASG acid, forming an intensely colored solution of the azo dye, identical with the product obtained when ASG acid is coupled with authentic 2-nitrodiazobenzene. Consequently, the basic component of the tarry substance is 2-nitroaniline. In addition, the presence of methyl alcohol in the aqueous solution was also demonstrated.

As a result, in contrast to the triazenesulfonates from 4-nitrodiazobenzene, 3-nitrodiazobenzene and

2,5-dichlorodiazobenzene, the triazenesulfonate from 2-nitrodiazobenzene separates, in addition to sulfuric acid, nitrogen and methyl alcohol, 2-nitroaniline, and not the corresponding symmetrical 2,2'-dinitrodiphenyltriazene.

d) 1-(4'-Nitro-2'-chloro)phenyl-3-methyltriazene-3-sulfonate (VI). The aqueous neutral solution of this triazenesulfonate on boiling cleaves the bisulfate ion even more easily than does the triazenesulfonate from 2-nitrodiazobenzene; together with nitrogen and methyl alcohol there is formed 4-nitro-2-chloroaniline, which was identified by diazotization and coupling with β-naphthol and ASG acid. Among the decomposition products, formed in the cleavage of the sulfonic group, the symmetrical diaryltriazene — 4,4'-dinitro-2,2'-dichlorodiphenyltriazene — is absent.

Determination of the Diazo Nitrogen Evolved During Hydrolytic Decomposition. The recrystallized triazene-N-sulfonate (V) (0.7127 g) was charged into the nitrometer flask and rubbed into a thick paste with several drops of water. After removal of the air from the apparatus with a current of CO_2 the flask contents were heated on the water bath to 60-65°. In a fairly short time brown stains appeared in the paste, within which swelling began due to the evolution of gas. Gradually the decomposition began to spread to the adjacent portions, and within several minutes all of the paste became brown, while the evolved nitrogen began to collect in the gas burette over potassium hydroxide.

As the result of decomposition there was obtained 48.4 ml of N_2 (22°, 750.8 mm), which corresponds to a diazo nitrogen content of 7.59 %, while theory for the amount of diazo nitrogen in $C_7H_6O_5N_4ClSK$ is 8.42 % (90.2 % of the theoretical amount).

Determination of the Amount of Cleaved Bisulfate. The residue from the reaction flask of the nitrometer was extracted with hot water. The hot orange colored aqueous extracts, after filtering off a small amount of tar, were cooled in ice water. The obtained yellow crystalline precipitate, which proved to be 4-nitro-2-chloroaniline, was filtered and washed. The filtrate and wash waters were acidified with hydrochloric acid and treated at the boil with a solution of barium chloride. There was obtained 0.4142 g of $BaSO_4$, which corresponds to a sulfur content of 7.96 %, while the theoretical amount of sulfur in $C_7H_6O_5N_4ClSK$ is 9.63 %. Consequently, the cleavage of the sulfonic group was 82.65 % complete.

Determination of the Amount of Formed Methyl Alcohol. The triazenesulfonate (V) (2.8347 g) was introduced into a distilling flask fitted with a Vigreaux column. The charge was moistened with 3 ml of water and heated up to 60-65°. The decomposition proceeded with greater violence than in the preceding experiment, inasmuch as a greater amount of material was taken. On conclusion of decomposition there was added to the flask 50 ml of water and 5 ml of concentrated sulfuric acid (to bind the amine), and the removal of the methyl alcohol by distillation was started.

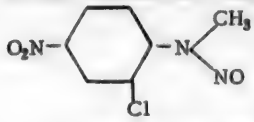
In measure with heating, the decomposition product in the distilling flask changed over more and more into a bright yellow orange colored solution. The undissolved portion of the product floated on the surface of the solution as brown oily stains. Despite the presence of sulfuric acid, the distillate was always yellow and deposited in the condenser and receiver lemon yellow crystals of steam volatile 4-nitro-2-chloroaniline. Apparently, the sulfate of this weakly basic amine is readily hydrolyzed with steam.

The approximately 25 ml of distillate obtained was redistilled through a small fractionation column. There was obtained 6.4381 g of distillate. Its density, determined with a pyknometer, was d_4^{15} 0.99485. From this it was calculated that 0.1503 g of methyl alcohol was present. Theory for the amount of product taken for the decomposition is 0.2730 g of alcohol, which means we found 55.06 % of this amount.

Determination of the Amount of Formed Amines. The triazenesulfonate (V) (0.4726 g) was rubbed in a beaker with several drops of water into a paste. After decomposition was accomplished by heating, to the obtained brown product was added an excess of concentrated hydrochloric acid and the mixture heated to nearly complete solution. The cooled hydrbchloric acid solution was diluted with 2 volumes of water and titrated with 0.1 nitrite solution. The consumption was 14.16 ml, while the theoretical should be 14.20 ml. Consequently, the formation of the amines was almost quantitative. The solution of the obtained diazo compound formed azo dyes when coupled with β-naphthol, R salt and ASG acid, which dyes are completely identical with those obtained in the coupling of the above azo components, with 4-nitro-2-chlorodiazobenzene.

The crude 4-nitro-2-chloroaniline, obtained as the result of hydrolytic decomposition of the triazenesulfonate, had m.p. 91-95° instead of the 107° given in the literature. Repeated recrystallization gradually raised the melting point to 98-99°, while the mixture with authentic 4-nitro-2-chloroaniline melted at 102-104°.

It was noted that toward the end in the diazotization of the investigated amine with nitrite in concentrated hydrochloric acid solution a precipitate always separates from the diazo solution, which after filtration, washing, drying and recrystallization is obtained as tiny yellow needles with m.p. 95°, giving, by the Liebermann test, the characteristic reaction for a nitroso product. According to the literature, 4-nitro-2-chloro-N-nitroso-N-methylaniline



is obtained as tiny yellow needles with m.p. 94.5-95.0° [7].

For identification purposes, the nitroso product, obtained in the treatment with nitrous acid of the amine formed in the decomposition of the triazene-N-sulfonate, was subjected to hydrolysis by boiling it with concentrated hydrochloric acid until solution was complete. The precipitate obtained on dilution with water, after recrystallization had m.p. 117°, exactly the same as the melting point given in the literature [7] for 4-nitro-2-chloro-N-methylaniline.

The final confirmation of the structure of the above described products was obtained by the N-methylation of 4-nitro-2-chloroaniline with dimethyl sulfate, using the method given in the literature for 4-nitroaniline [8]; on doing this the compound 4-nitro-2-chloro-N-methylaniline was obtained with m.p. 117°, failing to give a melting point depression when mixed with the amine obtained by the hydrolysis of the investigated nitroamine. Consequently, both 4-nitro-2-chloroaniline and its N-methyl derivative are simultaneously formed in the hydrolytic decomposition of 1-(4°-nitro-2'-chloro)phenyl-3-methyltriazene-3-sulfonate.

Influence of the Hydrolysis Conditions on the Yield of Amines. Experiment No. 1. The triazenesulfonate (V) (1.0244 g) was rubbed with water into a paste and then decomposed by heating on the water bath. The resultant brown decomposition product was dissolved in concentrated hydrochloric acid with heating, then cooled and treated with an excess of 10% nitrite solution. The obtained nitroso product, separated from the diazo compound by filtration through a porous glass filter, after washing and drying weighed 0.0440 g (6.63%).

Experiment No. 2. The triazenesulfonate (0.5680 g), recrystallized from water in the absence of ammonia, was allowed to stand in the air. Already on the following day brown spots appeared in the product, on the third day the triazene had become a moist brown substance, which, after another 3 days acquired a mustard yellow color and became dry. The product was dissolved in 15 ml of concentrated hydrochloric acid, diluted with 100 ml of water, cooled, and titrated with 0.1 N nitrite solution. The consumption of nitrite was 16.87 ml, which corresponds to a 98.8% formation of the amines theoretically possible for the given weight of triazene.

The nitroso product obtained from the acid diazo solution, after filtration, washing and drying, weighed 0.1305 g (35.5%).

Experiment No. 3. The triazenesulfonate (1.6723 g) was decomposed under the conditions of Expt. No. 2. The yield of nitroso product was 0.4015 g (37.04%).

SUMMARY

1. The salts of 1-aryl-3-methyltriazene-3-sulfonic acids are capable of undergoing hydrolytic cleavage of the sulfonic group with comparative ease. The lability of the bond between the nitrogen of the arylmethyltriazene and the sulfonic group increases with increase in the electrophilic properties of the substitutents in the benzene ring.

2. Arylmethyltriazenes are obtained as the result of hydrolytic cleavage of the sulfonic group from 1-aryl-3-methyl-triazene-3-sulfonic acids, which triazenes are unstable in acid medium and decompose into nitrogen, methyl alcohol and the arylamine.

3. In the cases where moderately electrophilic substituents are present in the aryl nucleus of 1-aryl-3-methyltriazene-3-sulfonic acids, then simultaneously with the decomposition reaction with the formation of arylamines there proceeds the reaction of cleavage into diazo compound and methylsulfamic acid, which leads to the formation of symmetrical diaryltriazenes as the final products.

4. On the example of 1-(4'-nitro-2'-chloro)phenyl-3-methyltriazene-3-sulfonate it was established that the methylaryltriazenes, intermediately formed as the result of cleavage of the sulfonic group, are also capable of decomposing into nitrogen and the N-methylarylmine. The presence of the least possible amount of water favors this type of decomposition.

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SOME N-DERIVATIVES OF AMINO ACIDS AND PEPTIDES

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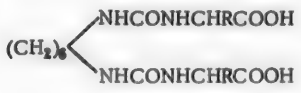
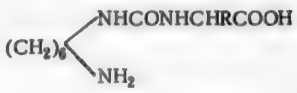
Up to now the separation of mixtures of amino acids and peptides has been quite a difficult problem. Even the extensive development of the new methods, like chromatography and electrophoresis on filter paper, does not always make possible the complete separation of a complex mixture. The preparative methods for the isolation of amino acids and peptides in the form of various derivatives have not lost their significance; for this reason searches for new substances, new derivatives of amino acids, and peptides, suitable for preparative and isolation purposes, possessing characteristic properties, are of interest from the viewpoint of investigating the composition and structure of proteins. In the present study a method is described for the preparation and characterization of hexamethylenebis-N-carbamyl derivatives of amino acids and peptides, which compounds have not been known in the literature.

1. Hexamethylenebis-N-carbamyl derivatives of amino acids. The reaction of hexamethylene diisocyanate with sodium salts of amino acids in aqueous medium at room temperature for several hours leads to the formation of hexamethylenebis-N-carbamyl derivatives, which are isolated by acidification of the solution. The reaction proceeds hardly at all with the free amino acids, even after a duration of several days. Hexamethylene diisocyanate, as we established, reacts with two molecules of amino acid to give a dicarboxylic derivative of the general formula (I). Reaction with one molecule of amino acid fails to take place under these conditions; consequently, the substance containing a free amino group together with a carboxyl group, corresponding to the formula (II), was not isolated.

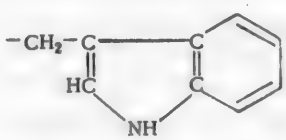


(I)

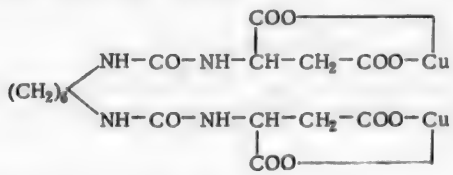


(II)

The following amino acid derivatives were obtained: hexamethylenebis-N-carbamylglycine [Formula (I), where R = H], hexamethylenebis-N-carbamyltryptophan [Formula (I), where R is



and hexamethylenebis-N-carbamylaspartic acid, isolated as the copper salt (III):



(III)

The obtained amino acid derivatives had definite melting points and were distinguished by their solubility, which permitted using them for identification purposes. In all cases, the ninhydrin and biuret reaction were negative.

2. Hexamethylenebis-N-carbamyl derivatives of peptides. On reacting hexamethylene diisocyanate with the sodium salts of glycyl peptides under the conditions described above for the amino acids, the following hexamethylenebis-N-carbamylpeptides were obtained: hexamethylenebis-N-carbamylglycylglycine

$$(CH_2)_6(NHCONHCH_2CONHCH_2COOH)_2,$$

hexamethylenebis-N-carbamylglycylglycylglycine

$$(CH_2)_6(NHCONHCH_2CONHCH_2CONHCH_2COOH)_2,$$

and hexamethylenebis-N-carbamylglycylglycylglycylglycine (or hexamethylenebisureidoacetylglycylglycylglycine)

$$(CH_2)_6[NHCONHCH_2CO(NHCH_2CO)_2NHCH_2COOH]_2.$$

The obtained peptide derivatives were distinguished by their melting points. The ninhydrin reaction was negative, the biuret reaction was positive.

Diketopiperazine (cycloglycylglycine) fails to react with hexamethylene diisocyanate under the above described conditions. From the reaction mass were isolated glycylglycine, diketopiperazine and polymer.

In all of the described cases a polymer, the reaction product of hexamethylene diisocyanate with water, was obtained as a secondary product, which substance was described by Bayer [1] as being a polyurea, with a highly branched chain. We isolated the white amorphous powder, which was insoluble in water, dilute alkalis, dilute acids, and organic solvents. The substance was dissolved by heating in concentrated formic, hydrochloric and nitric acids, and was reprecipitated on cooling the solution. The polymer dissolves when treated with zinc dust and dilute hydrochloric acid. When boiled with ninhydrin solution the deposit is colored purple. The biuret reaction is negative. The polymers isolated from the different reactions had a nitrogen content of 17.64 to 19.13%. The typical amount of amino nitrogen, determined by the Tsuverkalov method, was around 1%, which corresponds to around 2000 for the molecular weight.

EXPERIMENTAL

1. Preparation of hexamethylenebis-N-carbamylglycine. The sodium salt of glycine (2 g) was dissolved in 6 ml of water and 2 g of HM (hexamethylene diisocyanate) (1 mole of HM and 2 moles of glycine) was added with good stirring at room temperature. After 1 hour a white deposit appeared, after 3 hours the drops of HM disappeared (control placed under the microscope). The white deposit was filtered and washed well with water. The filtrate was acidified to litmus with glacial acetic acid. A large amount of a finely crystalline precipitate was obtained. The precipitate was filtered, washed with a small amount of cold water, and recrystallized from hot water. Dried in a vacuum desiccator and in a Fisher micro oven at 56°. Yield 0.8 g.

The white finely crystalline substance melts with decomposition at 175-176°; insoluble in organic solvents, is recrystallized from hot water.

Found %: N 15.4; equiv. (titration NaOH) 166.7. $C_{12}H_{22}O_6N_4 + 1\frac{1}{2}\ H_2O$. Calculated %: N 15.9; equiv. 172.1.

The derivatives of the other amino acids and peptides were obtained under analogous conditions.

2. Hexamethylenebis-N-carbamyltryptophan. The light straw-colored, finely crystalline precipitate in a sealed capillary sinters at 111-112°, and melts with decomposition at 125-130°. The substance is readily soluble in anhydrous methyl and ethyl acetate; insoluble in water, ether, benzene, acetone and chloroform.

Found %: N 13.28; equiv. 327. $C_{30}H_{36}O_6N_6 + 3H_2O$. Calculated %: N 13.44; equiv. 312.

3. Hexamethylenebis-N-carbamylaspartic acid. The free hexamethylenebis-N-carbamylaspartic acid is soluble in water, insoluble in anhydrous methyl alcohol, benzene and ether. Its copper salt was analyzed.

Found %: N 9.33. $C_{16}H_{22}O_{10}N_4Cu_2$. Calculated %: N 9.92.

4. Hexamethylenebis-N-carbamylglycylglycine. The white finely crystalline precipitate was obtained as oval aggregates of ill-defined elongated leaflets. M.p. 215° (with decomposition). Soluble in dilute alkali and insoluble in organic solvents.

Found %: N 18.85; equiv. 202.7. $C_{16}H_{28}O_8N_6$. Calculated %: N 19.4; equiv. 215.11.

5. Hexamethylenebis-N-carbamylglycylglycylglycine. The white finely crystalline substance is insoluble in organic solvents and soluble in dilute alkali. Negative ninhydrin reaction, positive biuret reaction. M.p. 227-229° (with decomposition).

Found %: N 21.48; equiv. 281.4. $C_{24}H_{34}O_{10}N_8$. Calculated %: N 20.66; equiv. 278.13.

6. Hexamethylenebis-N-carbamylglycylglycylglycylglycine. The white, finely crystalline substance melts with decomposition above 260°. Negative ninhydrin reaction, positive biuret reaction. Insoluble in organic solvents, sbluble in dilute alkali.

Found %: N 19.04; equiv. 301.5. $C_{24}H_{48}O_{12}N_{10}$. Calculated %: N 21.2; equiv. 330.16.

SUMMARY

1. The reaction of hexamethylene diisocyanate with amino acids and with peptides gives hexamethylene-bis-N-carbamyl derivatives of the general formula $(CH_2)_6(NHCONHCHRCOOH)_2$.

2. The compounds hexamethylenebis-N-carbamylglycine, hexamethylenebis-N-carbamylaspartic acid and hexamethylenebis-N-carbamyltryptophan were obtained, markedly differing in their solubilities and melting points.

3. The hexamethylenebis-N-carbamyl derivatives of glycylcycine, glycylglycylglycine and glycylglycyl-glycylglycine were obtained.

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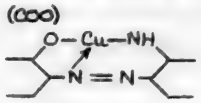
INTERNAL COMPLEX SALTS OF AZO COMPOUNDS

II. REACTION OF COPPER SALTS WITH SOME o-MONOAMINOAZO COMPOUNDS

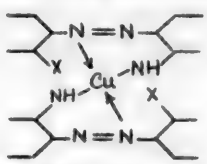
V. I. Mur

On the example of the reaction of cupric chloride with (o-methoxyphenylazo)-β-naphthol and 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-pyrazolone it was recently shown [1] that 1:1 complexes* of nonsulfonated o-monohydroxyazo compounds are capable of existence.

Up to now two types of copper complexes with o-monoaminoazo compound have been known [2]: the 1:1 complexes (I) [3], obtained from o-aminoazo compounds, in which in the second o-position to the azo group are contained the hydroxy-, carboxy- or other salt-forming groups, and the 1:2 complexes (II) [4-7], formed from o-aminoazo compounds not containing salt-forming groups in the second o-position to the azo group. Copper complexes with the second of the indicated types of azo compounds of the 1:1 type have not been known.



(I)

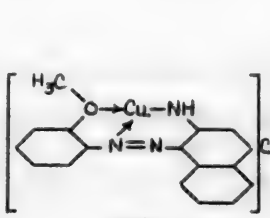


X=H, Cl, NO_2, OCH_3, CH_3, etc.

(II)

The reaction in alcohol medium of cupric chloride with (o-methoxyphenylazo)-β-naphthylamine and 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-aminopyrazole (not given in the literature) gave us complexes with a 1:1 composition, containing halogen. When these complexes are cleaved with dilute sulfuric acid, together with the resinification products, the original dyes are obtained, which permits assuming the presence of methoxyl groups in the complexes. Under the action of ammonia these complexes are converted into 1:2 complexes, losing 1 atom of copper and 2 atoms of chlorine for 2 molecules of original complex. The identical 1:2 complexes are obtained by treating the same azo compounds with an aqueous alcohol ammoniacal solution of copper sulfate; the reaction is accompanied by the formation of triazoles.

The analytical data and properties of the obtained complexes permit assigning to them the same structure that we had adopted earlier for the 1:1 complexes of o-methoxy-o'-hydroxyazo compounds and depicting it by formulas (III) for (o-methoxyphenylazo)-β-naphthylamine and (IV) for 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-aminopyrazole:



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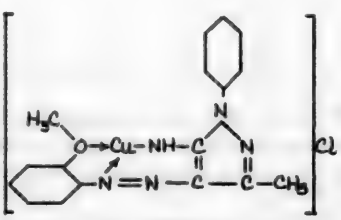


(IV)

Analogous 1:1 complexes for o-aminoazo compounds, containing in the o'-position to the azo group such atoms or groups as H, Cl, CH_3, $COOCH_3$ and NO_2, are not formed under the conditions used by us; only the formation of triazoles is observed.

* It is customary to designate the 1:1 complexes as being those complexes in which 1 atom of copper is present for 1 molecule of azo compound; in accord with this, the 1:2 complexes contain 1 atom of copper for 2 molecules of azo compound.

The ability of o-aminoazo compounds to be oxidized by copper salts to triazoles has long been known; as early as 1914 a patent [8] was granted on a method for the preparation of aryl triazoles. Later the method for obtaining the triazole ring by the oxidation of o-aminoazo compounds with copper salts found technical use in the production of light-fast azo dyes [9]. Certain investigators [10] attempted to study the influence of different substitutents in o-aminoazo compounds on the ease of oxidation of the latter to triazoles when heated in different solvents; however, in all cases a rule could not be established. The ability of o-aminoazo compounds to oxidize to triazoles has been investigated by Crippa [6], who, in studying the influence of certain substituents on the possibility of complex formation of o-aminoazo and o-hydroxyazo compounds with copper, cobalt and nickel, was unable to obtain the copper complex of (o-nitrophenylazo)-β-naphthylamine.

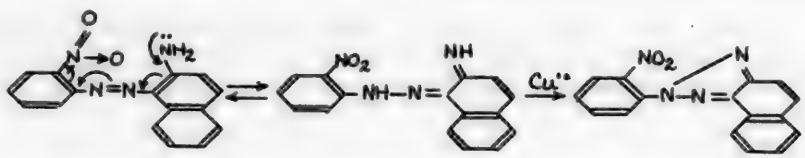
It appeared interesting to us to study the influence of substituents in o-aminoazo compounds on the ability of the latter to undergo complex formation and oxidation to triazoles, and to conduct the reaction with ammoniacal copper sulfate in aqueous alcohol medium. The reaction of the indicated reagents was conducted under the same conditions in all cases. The experimental results are given in the table. The obtained complexes were identified by the amount of copper in them;* the triazoles described in the literature – by the melting points, those not described – by the nitrogen content. The yield of the triazoles is not given in the table, inasmuch as its direct determination is impossible.

TABLE

Substituents in the benzene ring of the arylazo-β-naphthylamine	Yield of complex (in % of the theoretical)	Amount of decomposed complex (in % of the original)
H	68	7.9
o-OCH_3	50	2.9
o-CH_3	20	8.2
o-COOH	71	–
m-$COOCH_3$	65	13.7
p-$COOCH_3$	61	4.5
o-Cl	2	–
o-NO_2	0	–
m-NO_2	95	1.5
p-NO_2	87	1.9

If we exclude from the study the influence of the $COOCH_3$ group, due to its anomalous behavior (during complex formation the methyl radical is cleaved from the o-$COOCH_3$ group and the 1:1 complex that is formed corresponds to the carboxylic acid), then in the table the o'-substituents can be arranged in the order of increasing influence on the ability of o-aminoazo compounds to undergo oxidation (and consequently in the order of their decreasing influence on complex formation) as $OCH_3 < CH_3 < Cl < NO_2$. Phenylazo-β-naphthylamine is an exception.

On comparing the degree of electroaffinity of the enumerated substituents and the strength of their influence on the ability of o-aminoazo compounds to oxidize to triazoles, it can be concluded that a direct relationship exists between these properties. This becomes comprehensible if it is assumed that the oxidation of o-aminoazo compounds to triazoles passes through the hydrazone form, with the process being depicted in the following manner (taking into account the mutual influence of the atoms in the molecule):



The oxidation of m- and p-NO_2 groups as a function of their position exerts a lesser influence on the process.

The postulation made by some investigators [4] that the oxidation of o-aminoazo compounds proceeds through the stage of complex formation stands contradictory to our representations. The formation of the triazole methyl ester and copper complex of the carboxylic acid when ammoniacal copper is reacted with the methyl ester of

* The identification of the complexes, described in the literature, by the melting points cannot be considered conclusive, inasmuch as on heating they are transformed into triazoles before the melting point is reached; for example, on heating (p-nitrophenylazo)-β-naphthylamine in a capillary the substance gradually lightens, is converted into 2-(p-nitrophenyl)-naphtho-1',2':4,5-triazole and melts at 236°. Analogous transformations are suffered completely or in part by 2-(o-chlorophenyl)-naphtho-1',2':4,5-triazole, 2-(o-tolyl)-naphtho-1',2':4,5-triazole, etc..

o-carboxyphenylazo-β-naphthylamine supports our postulations.

The experimental results of determining the stability of the complexes under conditions close to those used for complex formation (Table) do not contradict the above said. The fact that in the decomposition products of certain complexes the original azo compounds were found together with the triazoles indicates that the formation of the triazoles could have proceeded by way of oxidation of the azo compounds obtained in the decomposition of the complexes. Consequently, the formation of triazoles, occurring in the reaction of o-aminoazo compounds with ammoniacal copper, can proceed by two methods – by the direct oxidation of the original azo compounds and by the oxidation of the azo compounds that are formed as the result of partial decomposition of the complexes successful in being formed. The relative amounts of formed complexes and triazoles depends on the ability of the o-aminoazo compounds to oxidize to triazoles and on the degree of stability of the complexes.

EXPERIMENTAL

The investigated o-aminoazo compounds were obtained by coupling the diazo compounds of the corresponding amines with the azo components in acid aqueous alcohol medium; into the formation of the complexes were introduced the azo compounds, purified by recrystallization from ethyl alcohol and identified by the melting points or by the nitrogen content. 1-Phenyl-3-methyl-5-aminopyrazole was obtained by the condensation of diacetonitrile with phenylhydrazine and subsequent cyclization of the obtained cyanoacetonephenylhydrazone [11]; despite the repeated attempts made to aminate 1-phenyl-3-methyl-5-pyrazolone we were unable to obtain the corresponding aminopyrazole by this method. The 1:1 complexes of copper with o-methoxyphenylazo-β-naphthylamine and 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-aminopyrazole were obtained under the earlier described conditions [1] used for the formation of the corresponding 1:1 complexes of o-methoxy-o'-hydroxyazo compounds, and were purified by washing with hot alcohol. We determined the amounts of copper and chlorine in the complexes by an earlier adopted method [1].

Copper salt of o-methoxyphenylazo-β-naphthylamine. Brownish red needles, m.p. 197°.

0.4324 g sub.: 11.38 ml 0.1 N $Na_2S_2O_3$. 0.1033 g sub.: 27.4 ml 0.01 N $AgNO_3$. 3.337 mg sub.: 0.329 ml N_2 (18°, 736.3 mm). Found %: Cu 16.73; Cl 9.42; N 11.20. $C_{17}H_{14}ON_3ClCu$. Calculated %: Cu 16.95; Cl 9.46; N 11.19.

The substance is cleaved by sulfuric acid with the formation together with tarry products, of the original dyes with m.p. 132-133° (the mixed melting point with the original dye failed to show a depression). The reaction with an aqueous alcohol solution of ammonia at room temperature is accompanied by the loss of 2 atoms of chlorine and 1 atom of copper per 2 molecules of complex, which is confirmed by the analysis data obtained for the reaction filtrate and the isolated complex, which complex was found to be identical with the 1:2 complex that is obtained when the same azo compound is reacted with ammoniacal copper sulfate in aqueous alcohol medium.

Found %: Cu 10.34. Calculated %: Cu 10.43.

Copper salt of 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-aminopyrazole. The original azo compound is obtained as yellow rhombic plates (from alcohol; under the microscope), m.p. 93.5-94.5°.

3.285 mg sub.: 0.658 ml N_2 (23.5°, 745.3 mm). Found %: N 22.61. $C_{17}H_{17}ON_5$. Calculated %: N 22.80.

When the azo compound is reacted in alcohol solution with cupric chloride the 1:1 complex is obtained as bright yellowish brown needles; m.p. 220° (with decomposition; determined by the method of introducing the capillary with substance into the preheated apparatus).

0.2290 g sub.: 5.59 ml 0.1 N $Na_2S_2O_3$. 2.950 mg sub.: 0.442 ml N_2 (20°, 742.1 mm). Found %: Cu 15.52; N 17.05. $C_{17}H_{16}ON_5ClCu$. Calculated %: Cu 15.69; N 17.28.

The complex is cleaved by sulfuric acid with the formation of the original dye. When treated with an alcoholic ammonia solution the substance is converted to the 1:2 complex, with the separation of chlorine and copper.

0.3456 g sub.: 5.02 ml 0.1 N $Na_2S_2O_3$. Found %: Cu 9.24. $(C_{17}H_{16}ON_5)_2Cu$. Calculated %: Cu 9.39.

Reaction of o-aminoazo compounds with ammoniacal copper sulfate. The mixture of an alcohol solution of the azo compound and an excess of aqueous ammoniacal copper sulfate solution was boiled for 1 hour, after which the mixture was diluted with cold water and the yield of complex was determined from the amount of complex bound copper in the obtained precipitate. After extracting the precipitate with hot ethyl alcohol the identity of the complex was determined from the copper content; the alcohol was removed from the extract by distillation and after recrystallization of the newly obtained precipitate the triazole was identified by its nitrogen content.

In the experiments with o-tolyl-, o-chlorophenyl- and the methyl ester of m-carboxyphenylazo-β-naphthylamine, together with the triazoles, the original dyes were isolated.

Under the conditions of the presented method were obtained the triazoles and 1:2 copper complexes of phenylazo-β-naphthylamine, (o-methoxyphenylazo)-β-naphthylamine, (o-tolylazo)-β-naphthylamine, (m- and p-nitrophenylazo)-β-naphthylamine (all described in the literature), (o-chlorophenylazo)-β-naphthylamine and the methyl esters of o-, m- and p-carboxyphenylazo)-β-naphthylamine (not described in the literature).

Copper salt of (o-chlorophenylazo)-β-naphthylamine. Dark crystals with greenish luster, under the microscope – dark rhombic prisms; on heating melts at 128°, which corresponds to the melting point of 2-(o-chlorophenyl)-naphtho-1',2':4,5-triazole.

0.0893 g sub.: 1.41 ml 0.1 N $Na_2S_2O_3$. Found %: Cu 10.04. $(C_{16}H_{11}N_3Cl)_2Cu$. Calculated %: Cu 10.18.

Copper salt, obtained from the methyl ester of (o-carboxyphenylazo)-β-naphthylamine. Reddish brown needles under the microscope, not melting up to 360°.

0.2048 g sub.: 5.79 ml 0.1 N $Na_2S_2O_3$. Found %: Cu 17.96. $C_{17}H_{11}O_2N_3Cu$. Calculated %: Cu 18.03.

When cleaved with sulfuric acid, a substance separates, after recrystallization from alcohol melting at 165-166° and failing to give a melting point depression with (o-carboxyphenylazo)-β-naphthylamine.

Copper salt of the methyl ester of (m-carboxyphenylazo)-β-naphthylamine. Brown plates; on heating is gradually converted into the corresponding triazole; melts below the melting point of the latter.

0.0940 g sub.: 1.43 ml 0.1 N $Na_2S_2O_3$. Found %: Cu 9.65. $(C_{18}H_{14}O_2N_3)_2Cu$. Calculated %: Cu 9.46.

Copper salt of the methyl ester of (p-carboxyphenylazo)-β-naphthylamine. Dark brown needles, behaves in the same manner as the preceding compound.

2-(o-Nitrophenyl)-naphtho-1',2':4,5-triazole. Pale pink needles, m.p. 124.3-125° (from the literature, 135°).

4.516 mg sub.: 10.962 mg CO_2; 1.420 mg H_2O. 2.982 mg sub.: 0.507 ml N_2 (22.6°, 739 mm). Found %: C 66.24; H 3.51; N 19.09. $C_{16}H_{10}O_2N_4$. Calculated %: C 66.21; H 3.45; N 19.31.

2-(o-Chlorophenyl)-naphtho-1',2':4,5-triazole. Colorless needles, m.p. 128-128.5°.

3.224 mg sub.: 0.429 ml N_2 (24°, 735 mm). Found %: N 14.78. $C_{16}H_{10}N_3Cl$. Calculated %: N 14.03.

Methyl ester of 2-(o-carboxyphenyl)-naphtho-1',2':4,5-triazole. Colorless needles, m.p. 217.5-218.5°.

3.120 mg sub.: 0.387 ml N_2 (18.5°, 731.7 mm). Found %: N 13.98. $C_{18}H_{13}O_2N_3$. Calculated %: N 13.86.

Methyl ester of 2-(m-carboxyphenyl)-naphtho-1',2':4,5-triazole. Colorless needles, m.p. 150-150.7°.

2.700 mg sub.: 0.340 ml N_2 (23°, 736.7 mm). Found %: N 14.08. $C_{18}H_{13}O_2N_3$. Calculated %: N 13.86.

Methyl ester of 2-(p-carboxyphenyl)-naphtho-1',2':4,5-triazole. Colorless needles, m.p. 181.5-182.5°.

2.790 mg sub.: 0.340 ml N_2 (21°, 737.6 mm). Found %: N 13.77. $C_{18}H_{13}O_2N_3$. Calculated %: N 13.86.

Behavior of copper salts on heating in an aqueous alcohol ammonia solution medium. A mixture of copper salt of the o-aminoazo compound and an aqueous alcohol ammonia solution was boiled for 1 hour, the mixture was filtered after cooling (the complex present in the precipitate was identified), the alcohol was distilled from the filtrate and in the aqueous solution, separated from the freshly obtained precipitate (in the latter was established the presence of the triazole and the azo compound), was determined the amount of copper, corresponding to the amount of decomposed complex (Table).

SUMMARY

1. A number of triazoles and complexes of copper with o-aminoazo compounds were obtained.

2. On the example of copper complex formation with (o-methoxyphenylazo)-β-naphthylamine and 1-phenyl-3-methyl-4-(o-methoxyphenylazo)-5-aminopyrazole was shown the possibility for the existence of 1:1 complexes of o-methoxy-o'-aminoazo compounds.

3. It was shown that in measure with increasing influence on the oxidation of o-aminoazo compounds the o-substituents can be arranged in the order: $OCH_3 < CH_3 < Cl < NO_2$.

4. Some evidence was presented in support of the postulation that the oxidation of o-aminoazo compounds to triazoles proceeds through the hydrazone form.

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REACTION OF NITRO DERIVATIVES OF BENZENESULFENAMIDE WITH CARBONYL COMPOUNDS

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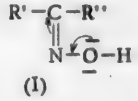
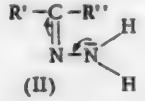
As a rule the unsymmetrical hydrazones, in contrast to the oximes, do not display geometric isomerism, although they contain the double bond C=N. This is explained [1] by the different influence of the OH (in oximes) and NH_2 (in hydrazones) groups on the "rigidity" of the C=N double bond.



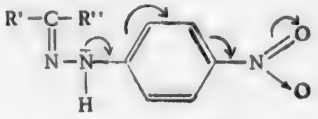
(I)



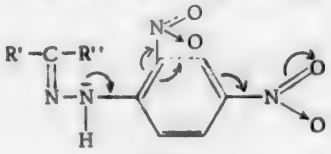
(II)

Due to the fact that nitrogen possesses less affinity for electrons than does oxygen, in the hydrazones (II) the displacement of the π-electrons is more pronounced than it is in the oximes (I); consequently, in the hydrazones due to the marked decrease in the double bond nature of the C=N bond the rotation around this bond proves to be slightly difficult and geometric isomerism is impossible.

If into the NH_2 group of the hydrazone a substituent is introduced, which substituent is strong enough to draw away in the opposite direction the unshared pair of electrons found in the NH_2 group, then it becomes possible to increase the degree of unsaturation of the atoms in the C=N grouping (the "rigidity" of the C=N bond) and as a result of this to effect the appearance of geometric isomerism.



(III)

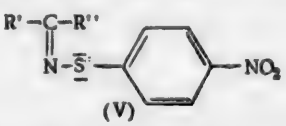


(IV)

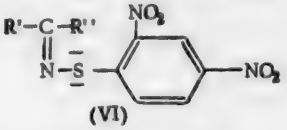
It was found that the p-nitrophenylhydrazones (III) still fail to display geometric isomerism, while at the same time it was found that certain 2,4-dinitrophenylhydrazones (IV) can be obtained in the form of two geometric isomers [1].

In increasing order of affinity for electrons the elements oxygen, sulfur and nitrogen can be arranged as follows: O (+17 kcal.), S (+48 kcal.) and N(–17 kcal.) [2-4]; consequently, with other conditions constant the sulfur analogs of the oximes (we will call them thioximes) should possess a lower "rigidity" of the C=N bond than the oximes, and a greater "rigidity" than the hydrazones.

In the present study we decided to verify these theoretical considerations by the method of synthesizing and studying the mono- and dinitrophenylthioximes, i.e. compounds having the structures (V) and (VI):



(V)



(VI)

Inasmuch as sulfur possesses a much greater electron affinity than does nitrogen, it can be expected that not only the dinitrophenyl derivatives of the thioximes (VI), but also the mononitrophenyl derivatives, (V), are capable of existing in the form of two geometric isomers.

To compare in this respect the oximes with the unsubstituted thioximes is as yet impossible, since the sulfur analog of hydroxyamine NH_2–SH, needed for the synthesis of the latter, does not exist. Its derivatives, needed for the synthesis of the thioximes (V) and (VI), belong to the class of amides of sulfenic acids or sulfenamides and are usually obtained by the reaction of sulfenyl halides with ammonia:

$$\longrightarrow R-S-Cl + NH_3 \rightarrow R-S-NH_2 + HCl.$$

In this manner we obtained both the described in the literature p-nitrobenzenesulfenamide [5] and the unknown 2,4-dinitrobenzenesulfenamide.

Up to the present time a special study of the reaction of sulfenamides with carbonyl compounds has not been made. However, a method is given in the literature for the condensation of certain sulfenamides with benzaldehyde and acetone; in this connection it is indicated that this reaction fails to proceed with other carbonyl compounds [6-10].

For studying the condensation of sulfenamides with carbonyl compounds we selected representatives of diverse carbonyl compounds: p-dimethylaminobenzaldehyde, acetone, acetoacetic ester, acetophenone, benzophenone and Michler's ketone. At the start we attempted to conduct the condensation of sulfenamides with p-dimethylaminobenzaldehyde under the conditions described in the literature, i.e. by boiling the reactants in alcohol. Negative results were obtained. After trying different reaction methods it was discovered that the condensation proceeds quite easily if the reactants are boiled in alcohol in the presence of a small amount of ammonium chloride. It was found that the latter is also a necessary catalyst for reaction in the case of other carbonyl compounds. To be sure, not all carbonyl compounds enter into this reaction with the same ease. The easiest of all to react with sulfenamides are the aldehydes, somewhat more difficult are the aliphatic ketones, considerably more difficult are the aliphatic-aromatic ketones and, finally, the purely aromatic ketones in general fail to react with sulfenamides under the given conditions.

On the matter of the rate of formation of thioximes it can be stated that this rate is considerably slower than it is for the formation of the corresponding oximes [11,12].

Similarily the oximes, the thioximes are decomposed under the influence of hydrochloric acid, forming the original carbonyl compound. As is known, the O-ethers of oximes are easily saponified by alkali [13], while at the same time the S-ethers of the thioximes fail to react with alkali.

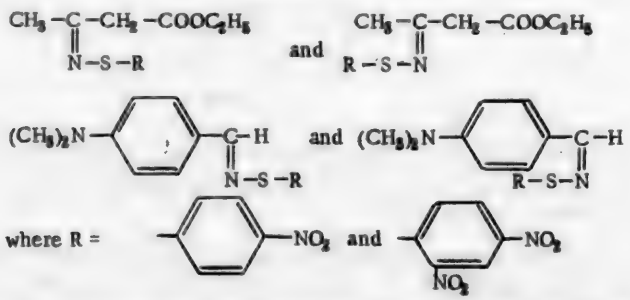
In studying the condensation of sulfenamides with carbonyl compounds we were able to show that certain unsymmetrical thioximes, containing the mononitrophenyl, as well as the dinitrophenyl radical, are actually capable of existing in the form of two isomers. We were able to obtain the isomeric thioximes by reacting p-nitrobenzenesulfenamide and 2,4-dinitrobenzenesulfenamide with p-dimethylaminobenzaldehyde and acetoacetic ester.

As was to be expected, in the reaction with acetone only single reaction products were obtained for each sulfenamide.

We were unable to obtain the thioximes of acetophenone in the form of two geometric isomers, although their existence appears possible to us. However, here it should be mentioned that the oximes of aryl alkyl ketones, as a rule, are also known only in one form [14]. At the present time only one aryl alkyl ketoxime, namely, the oxime of isobutyrophenonone. is known in two forms [15].

The thioximes obtained by us can all be recrystallized from the same solvent; in this connection they remain unchanged; this demonstrates the fact that we are not dealing with isomorphous substances. We were unable to use the cryoscopic method for determining the molecular weights of the isomers due to their poor solubility in benzene, nitrobenzene and other solvents, suitable for cryoscopy. Determination of the molecular weight by the Rast method gave the same values for isomeric thioximes, although these values differed considerably from those calculated for the formula.

In contrast to the corresponding hydrazones, in which a hydrogen atom is found attached to a nitrogen atom, our thioximes are devoid of hydrogen at the sulfur atom; consequently, for them the possibility of tautomerism, similar to the azo-hydrazone tautomerism, is eliminated. This gives us a right to believe that here we are actually dealing with geometric isomers of the thioximes.



As is known, certain O-ethers of the oximes by simple heating undergo the Beckmann rearrangement [13,16]. Our attempts to perform a similar rearrangement on the above enumerated S-ethers of thioximes remained unsuccessful.

It should be mentioned that we were unable to transform a single one of the four thioximes of acetoacetic ester into the corresponding heterocycle. For these reasons we cannot as yet assign a definite spatial configuration to the obtained geometric isomers of thioximes.

In all of the examined cases the formation of the labile isomer proceeded at a much faster rate than did the formation of the stable form. Thus, if a short reaction period was employed, then the labile isomer was predominantly obtained; in measure with increase in the reaction time the stable isomer began to accumulate. It was possible to determine the limits within which practically only the labile isomer is obtained, the mixture of labile and stable and, finally, only the stable isomer. The labile isomers of the thioximes have a lower melting point, a greater solubility in organic solvents and a deeper color than the stable isomers. Transformation of the labile isomers into the stable form is observed on boiling the labile isomers in alcohol, on heating them above the melting point, and on treating them with concentrated sulfuric acid. We were unable to demonstrate the reverse transition of stable isomers into the labile form. We failed to observe this transition even under prolonged exposure of the stable isomer to ultraviolet radiation, which, as is known, in certain cases effects the transition of stable oximes into the labile form [17].

The ability to obtain the stereoisomeric mononitrophenylthioximes confirms the fact that the sulfur in thioximes lowers the "rigidity" of the bond in C=N to a lesser degree than does the nitrogen in hydrazones. The latter are obtained in the form of stereoisomers only in the presence of two or three nitro groups in the phenylhydrazine molecule [1]. The question of whether this phenomenon of geometric isomerism will disappear in the case of unsubstituted phenylthioximes remains unanswered due to the inability of obtaining the unsubstituted benzenesulfenamide [18].

EXPERIMENTAL

Synthesis of 2,4-dinitrobenzenesulfenamide. 2,4-Dinitrobenzenesulfenyl chloride [19], obtained from 10 g of 2,2',4,4'-tetranitrodiphenyl disulfide [20] (this compound should not be dried due to its strongly explosive nature), is diluted with 200 ml of ether, and this suspension is added to 150 ml of 24% ammonia solution. A dark brown precipitate of 2,4-dinitrobenzenesulfenamide is formed. The ether is removed by evaporation; the precipitate is filtered, washed with water, and dried at 60-80°. Yield of crude product 7 g, m.p. 110-115°. After recrystallization from alcohol, m.p. 119-120°. Yield 65.5%. Dark yellow fine slender needles. Soluble in hot alcohol, chloroform, benzene and ethylene dichloride, poorly soluble in ether, practically insoluble in water. Stable in alkali solution, and under the action of hydrochloric acid it evolves ammonia and forms 2,2',4,4'-tetranitrodiphenyl disulfide.

0.1026 g sub.: 17.3 ml N_2 (20°, 762 mm). 0.0977 g sub.: 16.3 ml N_2 (18°, 757 mm). 0.1361 g sub.: 0.1661 g CO_2; 0.0316 g H_2O · 0.0917 g sub.: 0.1132 g CO_2; 0.0260 g H_2O · 0.0931 g sub.: 0.1042 g $BaSO_4$. 0.1341 g sub.: 0.1442 g $BaSO_4$. Found %: N 19.5, 19.3; C 33.3, 33.5; H 2.6, 3.1; S 15.1, 15.2; $C_6H_3O_4N_3S$. Calculated %: N 19.2; C 33.4; H 2.3; S 14.9.

Condensation of p-nitrobenzenesulfenamide with p-dimethylaminobenzaldehyde. a) Preparation of the labile isomer of the p-nitrophenylthioxime of p-dimethylaminobenzaldehyde. One gram of p-nitrobenzenesulfenamide and 1 g of p-dimethylaminobenzaldehyde were dissolved with heating in 40 ml of alcohol, a small amount of ammonium chloride was then added and the mixture was boiled for 10-15 minutes. On cooling the solution there separates 0.6 g (34%) of orange precipitate, m.p. 145-150°. Dilution of the filtrate with water results in the precipitation of unchanged p-nitrobenzenesulfenamide and p-dimethylaminobenzaldehyde. After recrystallization from 20 volumes of alcohol the condensation product melts at 154-155°. Tiny orange needle crystals. Readily soluble in chloroform and ethylene dichloride, soluble in hot alcohol, difficultly soluble in ether, insoluble in water.

0.0900 g sub.: 11.4 ml N_2 (18°, 748.5 mm). 0.1222 g sub.: 15.2 ml N_2 (20°, 753 mm). 0.1053 g sub.: 0.2304 g CO_2; 0.0486 g H_2O. 0.0977 g sub.: 0.2140 g CO_2; 0.0420 g H_2O. 0.0971 g sub.: 0.0773 g $BaSO_4$. 0.1279 g sub.: 0.1036 g $BaSO_4$. Found %: N 14.4, 14.2; C 59.5, 59.6; H 5.2, 4.8; S 10.8, 11.0. $C_{15}H_{15}O_3N_3S$. Calculated %: N 13.9; C 59.8; H 5.0; S 10.6.

b) Preparation of the stable isomer of the p-nitrophenylthioxime of p-dimethylaminobenzaldehyde. A solution of 1 g of p-nitrophenylbenzenesulfenamide and 1 g of p-dimethylaminobenzaldehyde in 40 ml of alcohol with a small amount of ammonium chloride was boiled for 4 hours. The precipitate obtained in the reaction process was periodically filtered from the hot solution, while boiling of the filtrate was continued. In this case only the stable isomer is obtained, m.p. 167-168°. Yield of product 0.9 g (51%). Boiling of the solution in excess of 4 hours fails to increase the yield of condensation product. The thioxime is recrystallized from chloroform. M.p. 172-173°. Bright red needlelike crystals, soluble in hot chloroform and ethylene dichloride, difficultly soluble in hot alcohol, practically insoluble in ether and water.

0.1224 g sub.: 15.1 ml N_2 (20°, 762 mm). 0.1106 g sub.: 13.2 ml N_2 (18°, 761 mm). 0.0800 g sub.: 0.1744 g CO_2; 0.0397 g H_2O. 0.0981 g sub.: 0.2147 g CO_2; 0.0461 g H_2O. 0.1129 g sub.: 0.0830 g $BaSO_4$. 0.1448 g sub.: 0.1166 g $BaSO_4$. Found %: N 14.2, 13.9; C 59.4, 59.6; H 5.48, 5.3; S 10.0, 11.0. $C_{15}H_{18}O_2N_2S$. Calculated %: N 13.9; C 59.8; H 5.0; S 10.6.

Condensation of 2,4-dinitrobenzenesulfenamide with p-dimethylaminobenzaldehyde. a) Preparation of the labile isomer of the 2,4-dinitrophenylthioxime of p-dimethylaminobenzaldehyde. A mixture of 1.2 g of 2,4-dinitrobenzenesulfenamide and 1.5 g of p-dimethylaminobenzaldehyde was dissolved with heating in 50 ml of alcohol, a small amount of ammonium chloride was added, and the solution was boiled for 10 minutes. On cooling the solution a precipitate separated as glistening bright red needle crystals. Yield 1.4 g (72.5%).

The product is recrystallized from 25 volumes of alcohol. M.p. 94-95°. Readily soluble in chloroform, ethylene dichloride, hot alcohol and benzene, difficultly soluble in ether, insoluble in water.

0.1294 g sub.: 18.5 ml N_2 (23.5°, 738 mm). 0.1300 g sub.: 18.5 ml N_2 (23°, 746 mm). 0.1691 g sub.: 0.3200 g CO_2; 0.0682 g H_2O. 0.1053 g sub.: 0.2008 g CO_2; 0.0424 g H_2O. 0.0951 g sub.: 0.0630 g $BaSO_4$. 0.0983 g sub.: 0.0645 g $BaSO_4$. Found %: N 15.8, 15.96; C 51.6, 51.8; H 4.5, 4.5; S 9.1, 9.0, $C_{15}H_{14}O_4N_4S$. Calculated %: N 16.2; C 52.02; H 4.04; S 9.2.

b) Preparation of the stable isomer of the 2,4-dinitrophenylthioxime of p-dimethylaminobenzaldehyde. A solution of 1.2 g of 2,4-dinitrobenzenesulfenamide and 1.5 g of p-dimethylaminobenzaldehyde in 50 ml of alcohol was boiled with a small amount of ammonium chloride for 4 hours, with periodic removal of the separated precipitate. Yield 1.7 g (88%), m.p. 184-185°. Further boiling of the solution fails to increase the yield. The product is purified by recrystallization from 40 volumes of chloroform. Dark red amorphous powder, m.p. 189-190°. Soluble in hot chloroform and ethylene dichloride, difficultly soluble in alcohol and ether, practically insoluble in water.

0.1217 g sub.: 17.3 ml N_2 (21°, 751 mm). 0.1008 g sub.: 14 ml N_2 (20°, 758 mm). 0.1391 g sub.: 0.2666 g CO_2; 0.0560 g H_2O. 0.1118 g sub.: 0.2140 g CO_2; 0.0439 g H_2O. 0.1420 g sub.: 0.0972 g $BaSO_4$. 0.1275 g sub.: 0.0891 g $BaSO_4$. Found %: N 16.1, 15.9; C 52.4, 52.1; H 4.5, 4.4; S 9.3, 9.4. $C_{15}H_{14}O_4N_4S$. Calculated %: N 16.2; C 52.02; H 4.04; S 9.2.

Condensation of p-nitrobenzenesulfenamide with acetone. A mixture of 1 g of p-nitrobenzenesulfenamide and 5 ml of acetone was boiled with 20 ml of alcohol and a small amount of ammonium chloride for 3 hours. On cooling there was obtained 0.9 g (75%) of orange precipitate, m.p. 145-151°.

After recrystallization from alcohol the condensation product is obtained as glistening yellow prisms with m.p. 174-175°. Soluble in hot alcohol, acetone, chloroform and ethylene dichloride, insoluble in water. A short boiling period gives the same product.

0.0742 g sub.: 8.2 ml N_2 (16°, 767.5 mm). 0.1106 g sub.: 11.6 ml N_2 (17°, 765.5 mm). 0.1378 g sub.: 0.2644 g CO_2; 0.0634 g H_2O. 0.1227 g sub.: 0.2327 g CO_2; 0.0552 g H_2O. Found %: N 13.1, 12.6; C 51.8, 51.7; H 5.15, 5.0. $C_9H_{10}O_2N_2S$. Calculated %: N 13.3; C 51.4; H 4.9.

Condensation of 2,4-dinitrobenzenesulfenamide with acetone. (Preparation of the 2,4-dinitrophenylthioxime of acetone). A mixture of 1 g of 2,4-dinitrobenzenesulfenamide and 5 ml of acetone was boiled with 20 ml of alcohol and a small amount of ammonium chloride for 1 hour. On cooling a yellow flocculent precipitate separated from solution, yield 0.8 g (83.5%), m.p. 132° (decomp.). Slender yellow needles. After recrystallization from alcohol the product melts with decomposition at 135°. Soluble in hot alcohol, chloroform, ethylene dichloride and acetone, insoluble in water.

0.1192 g sub.: 17 ml N_2 (18°, 760 mm). 0.1332 g sub.: 19.3 ml N_2 (18°, 759.5 mm). 0.1372 g sub.: 0.2214 g CO_2; 0.0464 g H_2O. 0.0719 g sub.: 0.1134 g CO_2; 0.0272 g H_2O. Found %: N 16.64, 16.8; C 42.6, 42.8; H 3.5, 4.2. $C_9H_9O_4N_3S$. Calculated %: N 16.5; C 42.3; H 3.7.

Condensation of p-nitrobenzenesulfenamide with acetoacetic ester. a) Preparation of the labile isomer of the p-nitrophenylthioxime of acetoacetic ester. A mixture of 1 g of p-nitrobenzenesulfenamide and 1 ml of acetoacetic ester was boiled with 30 ml of alcohol and a small amount of ammonium chloride for 1.5 hours. On cooling a cream-colored crystalline precipitate separates from solution, yield 0.3 g (18%), m.p. 100-102°. After recrystallization from 20 volumes of alcohol, m.p. 105.5-106°. Soluble in hot alcohol, chloroform and ethylene dichloride, insoluble in water.

0.1190 g sub.: 0.2240 g CO_2; 0.0532 g H_2O. 0.0949 g sub.: 0.1766 g CO_2; 0.0446 g H_2O. 0.1084 g sub.: 0.0876 g $BaSO_4$. 0.1236 g sub.: 0.1001 g $BaSO_4$. Found %: C 51.3, 50.8; H 4.9, 5.3; S 11.0, 11.1. $C_{12}H_{14}O_4N_2S$. Calculated %: C 51.06; H 4.9; S 11.34.

b) Preparation of the stable isomer of the p-nitrophenylthioxime of acetoacetic ester. A solution of 1 g of p-nitrobenzenesulfenamide and 1 ml of acetoacetic ester in 30 ml of alcohol with ammonium chloride was boiled for 4 hours. On cooling and prolonged standing a yellow flocculent precipitate separates, yield 1.2 g (73%), m.p. 137-139°. Recrystallization from 10 volumes of alcohol gives tiny bright yellow fluffy needles with m.p. 146-147°. The product is readily soluble in chloroform, hot alcohol and ethylene dichloride, insoluble in water.

0.1242 g sub.: 10.6 ml N_2 (20°, 758 mm). 0.1054 g sub.: 9.1 ml N_2 (22°, 764 mm). 0.1131 g sub.: 0.2115 g CO_2; 0.0509 g H_2O. 0.0984 g sub.: 0.1850 g CO_2; 0.0443 g H_2O. 0.0854 g sub.: 0.0723 g $BaSO_4$. 0.0959 g sub.: 0.0825 g $BaSO_4$. Found %: N 9.8, 9.9; C 51.03, 51.3; H 5.0, 5.0; S 11.6, 11.8. $C_{12}H_{14}O_4N_2S$. Calculated %: N 9.9; C 51.06; H 4.9; S 11.34.

Condensation of 2,4-dinitrobenzenesulfenamide with acetoacetic ester. a) Preparation of the labile isomer of the 2,4-dinitrophenylthioxime of acetoacetic ester. A solution of 1 g of 2,4-dinitrobenzenesulfenamide and 1 ml of acetoacetic ester in 40 ml of alcohol with ammonium chloride was boiled for 2 hours. After standing for a day a glistening orange precipitate separates from the cold solution in the form of long slender needles. Yield 1.1 g. Dilution of the filtrate with water gives another 0.2 g of substance. Total yield of product 86%. At 130° the substance turns yellow and then melts at 166-168°. The substance is recrystallized from 20 volumes of alcohol. It is soluble in chloroform and ethylene dichloride, difficultly soluble in methyl alcohol and ether.

0.0982 g sub.: 11.2 ml N_2 (20°, 762.5 mm). 0.1217 g sub.: 14.1 ml N_2 (20°, 762 mm). 0.0845 g sub.: 0.1410 g CO_2; 0.0357 g H_2O. 0.1061 g sub.: 0.1715 g CO_2; 0.0432 g H_2O. 0.1336 g sub.: 0.0979 g $BaSO_4$. 0.1115 g sub.: 0.0818 g $BaSO_4$. Found %: N 13.2, 13.4; C 44.4, 44.4; H 4.6, 4.5; S 9.99, 10.0. $C_{12}H_{13}O_6N_3S$. Calculated %: N 12.8; C 44.0 H 4.0; S 9.8.

b) Preparation of the stable isomer of the 2,4-dinitrophenylthioxime of acetoacetic ester. A solution of 1 g of 2,4-dinitrobenzenesulfenamide and 1 ml of acetoacetic ester in 40 ml of alcohol with ammonium chloride was boiled for 4 hours. On cooling, a bright yellow finely crystalline precipitate was obtained, m.p. 167-168°. Yield 1.3 g (86%). Recrystallization from 20 volumes of alcohol gives the product as yellow glistening pyramid crystals. Soluble in hot alcohol, chloroform and ethylene dichloride, difficultly soluble in ether.

0.1094 g sub.: 12.4 ml N_2 (18°, 762 mm). 0.0971 g sub.: 11.1 ml N_2 (20°, 762 mm). 0.1082 g sub.: 0.1744 g CO_2; 0.0420 g H_2O. 0.0845 g sub.: 0.1410 g CO_2; 0.0327 g H_2O. 0.1090 g sub.: 0.0809 g $BaSO_4$. 0.1211 g sub.: 0.0866 g $BaSO_4$. Found %: N 13.1, 13.2; C 43.9, 44.5; H 4.4; 4.4; S 10.1, 9.8. $C_{12}H_{13}O_6N_3S$. Calculated %: N 12.8; C 44.0; H 4.0; S 9.8.

Condensation of p-nitrobenzene sulfenamide with acetophenone. (Preparation of the p-nitrophenylthioxime of acetophenone). A mixture of 1 g of p-nitrobenzene sulfenamide and 2 ml of acetophenone was dissolved in 30 ml of alcohol, the addition of ammonium chloride was made and the mixture was boiled for 4 hours. At first, after partial cooling, there separates 0.2 g of finely crystalline brick-red precipitate from the warm solution, m.p. 174-175.5°. This precipitate is p,p'-dinitrodiphenyl disulfide.

On complete cooling of the filtrate there separates 0.55 g (34%) of yellow flocculent thioxime, m.p. 137-140°. The product is purified by recrystallization from 75 volumes of alcohol or 20 volumes of ethylene dichloride. The p-nitrophenyl thioxime of acetophenone is a yellow voluminous substance appearing as tiny slender needles, m.p. 151-152°. Soluble in chloroform, ethylene dichloride and hot alcohol, insoluble in water.

0.0974 g sub.: 8.6 ml N_2 (19.5°, 772 mm). 0.0893 g sub.: 7.9 ml N_2 (20°, 763 mm). 4.250 mg sub.: 9.540 mg CO_2; 1.720 mg H_2O. 0.1070 g sub.: 0.0918 g $BaSO_4$. 0.1285 g sub.: 0.1051 g $BaSO_4$. Found %: N 10.33, 10.2; C 61.26; H 4.52; S 11.7, 11.6. $C_{14}H_{12}O_2N_2S$. Calculated %: N 10.3; C 61.75; H 4.4; S 11.75.

Condensation of 2,4-dinitrobenzenesulfenamide with acetophenone. (Preparation of the 2,4-dinitrophenylthioxime of acetophenone). A mixture of 1 g of 2,4-dinitrobenzenesulfenamide and 2 ml of acetophenone was dissolved in 30 ml of alcohol, a small amount of ammonium chloride was added, and the mixture was boiled for 5 hours. The precipitate obtained in the reaction was periodically removed by filtration. Yield 0.4 g (27%), m.p. 179-180°. Glistening greenish-brown fine crystals. Difficultly soluble in hot alcohol, more readily soluble in chloroform and ethylene dichloride.

0.1166 g sub.: 13.0 ml N_2 (19°, 767.5 mm). 0.1058 g sub.: 12.3 ml N_2 (19°, 765 mm). 0.1316 g sub.: 0.2539 g CO_2; 0.0486 g H_2O. 0.1135 g sub.: 0.2191 g CO_2; 0.0386 g H_2O. Found %: N 13.0, 13.5; C 52.6, 52.7; H 3.9, 3.8. $C_{14}H_{11}O_4N_3S$. Calculated %: N 13.2; C 53.0; H 3.5.

SUMMARY

1. The previously unknown 2,4-dinitrobenzenesulfenamide was obtained and characterized.

2. In the process of studying the condensation of sulfenamides with carbonyl compounds a number of new compounds, the thioximes, were obtained.

3. The geometric isomerism of the thioximes of unsymmetrical carbonyl compounds was revealed for the first time. The geometric isomers of the p-nitrophenylthioximes and 2,4-dinitrophenylthioximes of p-dimethylaminobenzaldehyde and acetoacetic ester were obtained. The conditions were studied for the formation of the geometric isomers, their properties, and also the conditions for the transformation of the labile isomers into the stable forms.

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* See Consultants Bureau English Translation, p. 123.

ADDITION OF IODINE CHLORIDE TO ASYMMETRICAL DIPHENYLETHYLENE HYDROCARBONS

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Study of the reaction of iodine chloride with 1,1-diphenylpropene-1 [1] demonstrated that it gives 1,1-diphenyl-2-chloropropene-1, in all probability as the result of prior formation of 1-iodo-1,1-diphenyl-2-propene, cleaving at the moment of hydrogen iodide reaction. This reaction differs, by its reverse order of addition (contrary to Markovnikov's rule), from the reaction of iodine chloride and 1,1-diphenylethylene, studied by the same authors.

In this connection it appeared to us to be of interest to study the reaction of chloriodide with 1,1-di-p-tolylpropene-1 (I), and to determine whether the two methyl groups in the para-position are capable of compensating for the opposing influence of the methyl group adjoining the double bond, and whether this might go so far as to reverse the order of addition. The effect of these two methyl groups should be felt through the phenyl ring (Nathan-Backer effect) [2].

The initial hydrocarbon, not described in the literature, was obtained by dehydration of di-p-tolyl-ethylcarbinol by the Allen and Converse method [3]. Preliminary experiments showed the reaction mixture to contain the initial di-p-tolyl ketone, from which it proved impossible to obtain the hydrocarbon by distillation; the di-p-tolylpropene was therefore further purified by chromatographic filtration through a layer of active aluminum oxide.

The reaction proceeded by reaction of at least two moles of iodine chloride with one of hydrocarbon, accompanied by separation of crystalline iodine and hydrogen chloride. Distillation of the reaction mixture gave a yellow oil containing the halogen. Qualitative analysis of the product after mineralization by the Carius method showed the halogen to be chlorine; no iodine was revealed either by macroanalytical or microcrystallographic reaction.

Part of the reaction mixture obtained was purified by selective adsorption in a column with active aluminum oxide. Separation and isolation of the reaction mixture components was performed by flushing the adsorption column with equal quantitites of solvent of increasing levels of polarity, and condensing the solvent of each fraction separately. The result of chromatographic analysis gave 2 maxima. The resinous substance which gave the second maximum was not subjected to further study. The substance which gave the first maximum was selectively adsorbed twice more for higher purification, and distilled in vacuum at 0.5 mm. The results of qualitative Carius analysis of the main fraction for presence of halogen corresponded to the formula for monochloroditolylpropene. The product subjected to analysis was a yellow oil, crystallizing upon long standing.

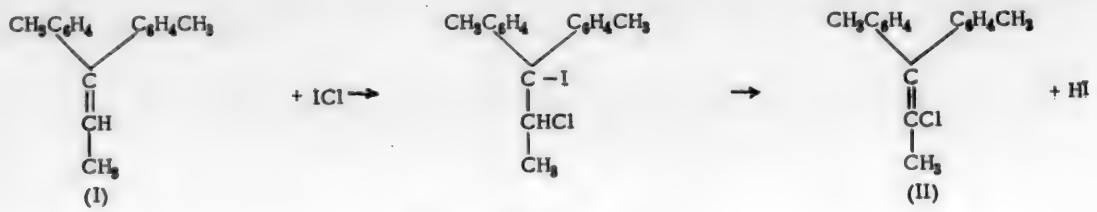
A portion of the reaction mixture, vacuum distilled, was used to determine the structure of the halogen derivative. The refractive index of this product, determined at two different temperatures, equalled that of the substance subjected to analysis. In the ozonization products of the substance we found di-p-tolyl ketone, a small quantity of methyl-p-tolyl ketone and p-tolylic acid.

As the presence of two isomers may result from the presence of isomers in the initial hydrocarbon, the latter was subjected to oxidation by equivalent quantities of chromium trioxide in a sulfuric acid medium. Di-p-tolyl ketone and acetic acid were found in the oxidation products.

The experiments performed made it possible to establish that 1,1-di-p-tolylpropene-1 reacts with iodine chloride to form 1,1-di-p-tolyl-2-chloropropene as the main product, and, with it, 1,2-p-tolyl-1-chloro-propene-1 in considerably smaller quantities.

The production of 1,1-di-p-tolyl-2-chloropropene-1 (II), is most probably to be explained in terms of the addition of iodine chloride to the initial hydrocarbon, contrary to Markovnikov's rule, with subsequent cleavage of hydrogen iodide as shown at the top of the next page.

1,2-Di-p-tolyl-1-chloropropene-1 was obtained as a result of molecular regrouping. It is of interest to clarify the chemistry of this regrouping and, in particular, to determine whether it occurs at the time of the reaction or at the stage of separation of the product from the reaction mixture.



(I) (II)

$$HI + ICl \rightarrow I_2 + HCl.$$

The present study was undertaken at the suggestion of T. I. Temnikova, to whom I express my gratitude.

EXPERIMENTAL

Synthesis of 1,1-di-p-tolylpropene-1. Di-p-tolyl ketone was obtained from 90 g anhydrous aluminum chloride, 280 ml dry tetrachloromethane and 142 ml toluene [5], with a 23% yield of the pure product, m.p. 94-95°. Di-p-tolylethylcarbinol was obtained by the method of these same authors from 12 g magnesium in 20 ml dry ether, 71.5 g ethyl bromide in 100 ml anhydrous ether, and 54 g di-p-tolyl-ketone. Dehydration of the raw carbinol was effected by 20% sulfuric acid with heating of the mixture to boiling for 1.5 hours. The mixture was subjected to ether extraction. Upon distillation of the ether the oil crystallized as it cooled. The yield of pure hydrocarbon was 43% of the theoretical, in terms of ketone used. Colorless crystalline substance, B. p. 199-200°/24 mm, 168-169°/9mm, m.p. 37-38°, n_D^{40} 1.5790. Soluble in all organic solvents.

0.03480 g sub.: 0.11692 g CO_2; 0.02521 g H_2O. 0.03423 g sub.: 0.11502 g CO_2; 0.02433 g H_2O. Found %: C 91.69, 91.70; H 7.92, 7.95. $C_{17}H_{18}$. Calculated %: C 91.84; H 8.16.

40 g hydrocarbon was filtered through 80 g aluminum oxide, Brockman activity 1, prepared according to [6], and filtered through a screen of 246 mesh per sq. cm. The column was filled by the wet process. The adsorbed matter was washed out with 80 ml petroleum ether. The rate of filtration was 1 drop per second.

Oxidation of 1,1-di-p-tolylpropene-1. 1.5 g hydrocarbon, 0.90 g chromium oxide and 12 ml 80% sulfuric acid were mixed together. The reaction mixture was heated to 50° with constant stirring for 5 hours. The mixture was carefully diluted with water to 15% of the amount of sulfuric acid and was subjected to ether extraction. The aqueous solution was brought to alkaline reaction and evaporated to dryness. The substance gave a positive cacodyl reaction. The ether extract was treated with 10% caustic soda. The alkaline solution was concentrated and acidified with sulfuric acid. The remaining ether solution was dried, the ether driven off, and the oily residue crystallized. A portion of the crystalline mass was filtered off with suction on a porous plate and recrystallized from alcohol. M.p. 93-94°. A sample mixed with pure di-p-tolyl ketone, m.p. 94-95°, melted at 94-95°.

The crystalline mass was put through distillation with water vapor to determine whether it contained methyl-p-tolyl ketone. The first few milliliters of distillate were treated with an acetic acid solution of semicarbazide; carbazone did not appear out of the solution even after long standing.

The remaining portion of the aqueous distillate was extracted with ether. After ether extraction a saturated solution of 0.4 g hydroxylamine chloride and 0.8 g sodium hydroxide was added to the residue, which was processed according to [7]. Upon recrystallization from alcohol, the product melted at 159°. A sample mixed with known di-p-tolyl ketoxime, m.p. 162-162.5°, melted at 160°.

Synthesis of monochloroditolylpropene. 24.11 g hydrocarbon purified by selective adsorption, n_D^{40} 1.5838, was dissolved in 50 ml dry chloroform. Iodine chloride was obtained by passing a current of dry chlorine over 145 g crystalline iodine and distilling the reaction mixture [4]. At room temperature and with constant stirring, 55.84 g iodine chloride, b.p. 101-104°, dissolved in 50 ml dry chloroform, was added to the hydrocarbon. The reaction was accompanied by evolution of heat in the reaction mixture, and liberation of hydrogen chloride and crystalline iodine. After standing for 3 days, the reaction mixture was washed with a 20% solution of sodium hyposulfite to decoloration, dried, and the solvent driven off in vacuum. The raw product consisted of a heavy dark oil.

10 g reaction mixture was put through threefold selective adsorption by aluminum oxide. The adsorbed substance was washed out successively with petroleum ether, a 1:1 petroleum ether and benzene mixture, benzene, and chloroform. The four fractions n_D^{20} 1.5936, 1.5935, 1.5935 and 1.5934, respectively, were further purified by distillation in vacuum. Yellow oil, B.p. 133-135°/0.5 mm, n_D^{20} 1.5938; n_D^{45} 1.5822.

0.18787 g sub.: 0.10335 g AgCl. 0.18363 g sub.: 0.10100 g AgCl. Found %: Cl 13.61, 13.61. $C_{17}H_{17}Cl$. Calculated %: Cl 13.81.

The substance underwent partial crystallization in the course of two months. Filtered by suction through a porous plate, it melted at 43.5-44°.

Ozonization of monochloroditolylpropene. 0.98 g of the substance obtained by distilling a portion of the reaction mixture was subjected to ozonization. B.p. 140-142°/ 0.5 mm, n_D^{20} 1.5838, n_D^{48} 1.5823. After standing for a long time, this substance underwent partial crystallization; suction filtered through a porous plate, it melted at 43°. A sample mixture with the crystalline product, m.p. 43.5-44°, isolated from the substance analyzed, melted at 43-44°. Ozone was passed through a solution of the substance in chloroform for 4 hours with cooling to −15°. After the solvent had been driven off, the ozonide was decomposed by water in presence of 0.4 g calcium carbonate with heating on a water bath for 4 hours.

Neutral products were driven off after alkalization of the solution with water vapor. The oil remaining after distillation of the ether, crystallized. After fourfold crystallization from alcohol, the substance weighed 0.1 g and melted at 94°. A sample mixed with pure di-p-tolyl ketone, m.p. 94-95°, also melted at 94-95°. Semicarbazide in acetic acid solution was added to the alcoholic filtrate. An insignificam amount of precipitate came down, which melted at 200° after crystallization from alcohol. A sample mixture with known methyl-p-tolyl semicarbazone, m.p. 202.5-203.5° [8] melted at 201-202°. After the neutral products had been driven off, the alkaline solution was acidified until a strongly acid reaction was obtained. A small amount of precipitate was obtained which melted at 179°. In mixture with p-tolylic acid prepared according to [9], (m.p. 180°), it melted at 179°.

After the precipitate was separated out, the acid solution was brought to highly alkaline reaction and concentrated by evaporation; this brought down a precipitate which was dissolved in water, slightly alkalized by ammonia and was then precipitated at 70° by a calcium chloride solution. The precipitate was filtered, washed with water and dissolved in 2N sulfuric acid. The action of the solution in reducing potassium permanganate demonstrated the presence of oxalic acid.

To demonstrate the presence of acetic acid in the form of its ester with p-bromobenzoylcarbinol, 1 g p-bromophenacyl bromide was added to the acid filtrate [10, 11]. However, the reaction mixture became resinous, and attempts to separate the specific reaction product by means of benzene extraction and distillation of the benzene solution with water vapor did not prove successful.

SUMMARY

1. 1,1-Di-p-tolylpropene-1 was synthesized for the first time.

2. It was determined that reaction of 1,1-di-p-tolylpropene-1 with iodine chloride results in 1,1-di-p-tolyl-2-chloropropene-1 as the main product, with small quantities of 1,2-di-p-tolyl-1-chloro-propene-1. The second product is the result of molecular rearrangement.

3. The presence of methyl groups in the para position of the phenyl nuclei of 1,1-diphenylpropene-1 does not affect the picture of iodine chloride addition to this asymmetrical diarylethylene hydrocarbon.

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THE SYNTHESIS OF SECONDARY 6-QUINOLYLCARBINOLS

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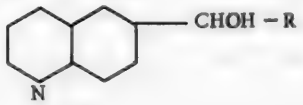
Continuing the study of the chemical properties of 6-quinolylaldehyde [1], we performed the Grignard reaction with its alkyl and aryl halide derivatives, obtaining secondary 6-quinolylcarbinols (I)



(I)

The literature contains a reference to Grignard synthesis of secondary 8-quinolylcarbinols [2]. 8-Quinolylmethyl-, ethyl- and phenyl- carbinols were obtained (with yield to 60% in the latter case; not indicated in the two former); oxidation of the carbinols with chromium trioxide and potassium bichromate synthesized the homologous 8-quinolyl ketones (yields not indicated).

We synthesized 6-quinolylmethylcarbinol by reacting 6-quinolylaldehyde with methylmagnesium iodide. Heating the carbinol with iodomethane and bromoethane gave the homologous alkyl halides. Oxidation of carbinol with chromium trioxide in glacial acetic acid solution yielded 6-quinolylmethyl ketone.

Reaction of 6-quinolylaldehyde with ethylmagnesium iodide synthesized 6-quinolylethylcarbinol as an oily liquid. 8-Quinolylethylcarbinol, synthesized previously [2], is also an oily liquid. The carbinol was identified in the form of its picrate and alkyl halides. Oxidation of carbinol by chromium trioxide in glacial acetic acid solution yielded 6-quinolylethyl ketone. Unlike 8-quinolylethyl ketone, an oily liquid [8], 6-quinolylethyl ketone came down as colorless crystals, m.p. 76-77°.

Reaction of 6-quinolylaldehyde with phenylmagnesium bromide synthesized 6-quinolylphenylcarbinol. Heating of carbinol with iodomethane and bromoethane gave the homologous alkyl halides. Oxidation of carbinol with chromium trioxide produced 6-quinolylphenyl ketone. Reaction of 6-quinolylaldehyde with α-naphthylmagnesium bromide gave 6-quinolyl-α-naphthylcarbinol. Long heating of carbinol with iodomethane gave its iodomethylate; the bromoethylate could not be obtained even after long heating of carbinol with bromoethane.

EXPERIMENTAL

Synthesis of 6-quinolylmethylcarbinol. 12.7 g aldehyde (anhydrous 6-quinolylaldehyde, m.p. 75-76°, was used in all experiments) in 200 ml dry ether was added in 30 minutes, drop by drop, with water cooling, to an ether solution of methylmagnesium iodide (3.2 g metallic magnesium filings*, 50 ml dry ether, 17.6 g – 1.55 mole – iodomethane, the reaction was maintained for an hour with heating on a water bath. 50 ml water and dilute (1:1) hydrochloric acid were added at cooling until acid reaction. The ether solution was separated out and washed with water, which was added to the acid solution; distillation of the ether left an insignificant residue. The acid solution was washed with ether and then neutralized with 16% ammonia to alkaline reaction upon cooling. After salting out with table salt, exhaustive extraction with ether was performed; after drying with sodium sulfate, the ether was driven off. The residue was a thick oily liquid that crystallized upon standing. 7.3 g (52%) 6-quinolylmethylcarbinol, m.p. 64-65°, was obtained; upon recrystallization from alcohol (upon evaporation of the latter) with activated charcoal, the m.p. was 69-71°. The carbinol dissolved readily in the ordinary organic solvents, but to an insignificant degree in light gasoline.

0.1816 g sub.: 11.22 ml NaOH (T 0.003634).** Found %: N 7.86. $C_{11}H_{11}ON$. Calculated %: N 8.09.

The picrate, obtained in alcohol solution and recrystallized from glacial acetic acid, consisted of light

* In all experiments, activated with iodine crystals.

** The nitrogen content was determined by the Kjeldahl method; NaOH had the same titer in every analysis.

yellow crystals, m.p. 176-177°.

Effect of alkyl halides upon 6-quinolylmethylcarbinol.

a) 0.54 g carbinol and 0.8 g iodomethane were heated for 30 minutes on a boiling water bath. Recrystallization from 1.5 ml ethyl alcohol gave 0.71 g (72.4%) 6-quinolylmethylcarbinol iodomethylate, light yellow crystals, m.p. 176-177°. The substance dissolved in water and alcohol but not in dry ether.

0.1224 g sub.: 0.0910 g AgI Found %: I 40.19. $C_{12}H_{14}ONI$. Calculated %: I 40.28.

b) 0.1 g carbinol and 0.3 g bromoethane were heated in a sealed tube for 2 hours at 90-95°. After evaporation of the bromoethane the residue was dissolved in a small quantity of alcohol; the bromoethylate crystallized upon evaporation of the alcohol (in a desiccator over paraffin and calcium chloride). After washing in dry ether the crystals had an m.p. of 143° (with softening), and weighed 0.12 g (63.1%); they dissolved in water and alcohol, but not in dry ether.

0.0656 g sub.: 0.0440 g AgBr. Found %: Br 28.54; $C_{13}H_{16}ONBr$. Calculated %: Br 28.33

Oxidation of 6-quinolylmethylcarbinol. 3.1 chromium trioxide was added, little by little, in 30 minutes, to 4.1 g carbinol, dissolved in 20 ml glacial acetic acid, with heating on a boiling water bath; heating continued another 30 minutes. The reaction mixture was poured into 150 ml water and neutralized with solid sodium carbonate; the reaction product was extracted with ether. Drying with sodium sulfate and driving off of the ether left a thick liquid that crystallized upon standing. 1.6 g 6-quinolylmethyl ketone was isolated (39.5%); after recrystallization from alcohol with activated charcoal it appeared as colorless crystals, m.p. 75-76°. The ketone dissolved readily in the usual organic solvents.

0.1526 g sub.: 10.02 ml NaOH. Found %: N 8.35. $C_{11}H_9ON$. Calculated %: N 8.18.

The picrate obtained in alcohol solution consisted of light yellow crystals, m.p. 236°.

Effect of iodomethane upon 6-quinolylmethyl ketone. 0.35 g ketone and 0.6 g iodomethane were heated on a boiling water bath for 30 minutes. 6-quinolylmethyl iodomethylate was obtained in yield of 56.2% upon recrystallization from alcohol and glacial acetic acid, in the form of golden yellow crystals, m.p. 225°. The iodomethylate dissolved in water and alcohol, but not in dry ether.

0.1002 g sub.: 0.0746 g AgI Found %: I 40.25. $C_{12}H_{12}ONI$. Calculated %: I 40.54.

Synthesis of 6-quinolylmethyl phenylhydrazone. 0.2 g ketone and 0.15 g phenylhydrazine in 1 ml ethyl alcohol were heated for 30 minutes on a boiling water bath. Evaporation of the alcohol left 0.2 g dark yellow crystals. Upon recrystallization from benzene and a few drops of alcohol the phenylhydrazone precipitated as orange crystals, m.p. 166°, which dissolved freely in alcohol but slightly in benzene.

0.0850 g sub.: 10.87 ml NaOH. Found %: N 16.27. $C_{17}H_{15}N_3$. Calculated %: N 15.96.

Synthesis of 6-quinolylethylcarbinol. 15.6 g aldehyde in 250 ml dry ether was added in 45 minutes, drop by drop, with water cooling, to an ether solution of ethylmagnesium iodide (3.7 g metallic magnesium, 50 ml dry ether, 23.2 g −1.5 mole− iodomethane); the reaction was continued for an hour with heating on a water bath. Appropriate treatment gave 6-quinolylethylcarbinol as 14.2 g of a thick liquid; the weight of the carbinol was 12.1 g (65.1%) in terms of the picrate produced.

0.85 g picric acid in 3.5 ml alcohol was added to 0.56 g carbinol dissolved in 2.5 ml ethyl alcohol. Upon heating the picrate emerged as dark yellow crystals, m.p. 151-152° (1.06 g); m.p. upon recrystallization from alcohol was 152°.

0.3825 g sub.: 39.60 ml NaOH. Found %: N 13.17. $C_{12}H_{13}ON \cdot C_6H_3O_7N$. Calculated %: N 13.46.

Effect of alkyl halides on 6-quinolylethylcarbinol.

a) 0.67 g carbinol and 0.9 g iodomethane were heated for 30 minutes over a boiling water bath. Recrystallization from alcohol gave 1 g (84.7%) yellow 6-quinolylethylcarbinol iodomethylate crystals, m.p. 165-166°. They dissolved in water and alcohol, but not in dry ether.

0.1078 g sub.: 0.0772 g AgI. Found %: I 38.71. $C_{13}H_{16}ONI$. Calculated %: I 38.81.

b) 0.86 g carbinol and 1 g bromoethane were heated for 1.5 hours at 90-100° in a sealed tube. Washing with dry ether gave 0.85 g (62.2%) 6-quinolylethylcarbinol bromoethylate as light-colored crystals, m.p. 168°. They dissolved in water and alcohol but not in dry ether.

0.2384 g sub.: 0.1530 g AgBr. Found %: Br 27.31. $C_{14}H_{18}ONBr$. Calculated %: Br 26.99.

Oxidation of 6-quinolylethylcarbinol. 4.2 g chromium trioxide was added, bit by bit, in 2 hours with heating on a boiling water bath, to 7 g carbinol dissolved in 2.5 ml glacial acetic acid. Processing gave 3.0 g 6-quinolylethyl ketone (43.3%) as light yellow crystals, m.p. 76°. Recrystallization from a small amount of alcohol with long cooling gave colorless crystals, m.p. 76-77°. The ketone dissolved readily in the common organic compounds.

0.3236 g sub.: 18.60 ml NaOH. Found %: N 7.31. $C_{12}H_{11}ON$. Calculated %: N 7.56.

The picrate obtained in alcohol solution and recrystallized from a mixture of alcohol and glacial acetic acid, consisted of light yellow-green crystals, m.p. 209°.

Effect of iodomethane on 6-quinolylethyl ketone. 0.5 g ketone and 1 g iodomethane were heated for 30 minutes over a boiling water bath. Recrystallization from alcohol gave dark yellow crystals, iodomethylate of 6-quinolylethyl ketone, (45.5% yield), m.p. 204°; soluble in water and alcohol, but not in dry ether.

0.1796 g sub.: 0.1280 g AgI Found %: I 38.52. $C_{13}H_{14}ONI$ Calculated %: I 38.47.

Synthesis of 6-quinolylethyl phenylhydrazone. 0.5 g ketone and 0.35 g phenylhydrazine were heated for an hour in 1.5 ml alcohol on a boiling water bath; the thick liquid remaining upon evaporation of the alcohol crystallized upon addition of a few drops of benzene. Recrystallization from a small amount of alcohol and benzene gave yellow crystals of the phenylhydrazone, m.p. 134-135°.

0.1168 g sub.: 14.14 ml NaOH. Found %: N 15.40. $C_{18}H_{17}N_3$. Calculated %: N 15.16.

Synthesis of 6-quinolylphenylcarbinol. 15 g aldehyde in 230 ml dry ether was added in 40 minutes, by drops, with water cooling, to an ether solution of phenylmagnesium bromide (2.5 g metallic magnesium, 50 ml dry ether, 16 g freshly-distilled bromobenzene); the reaction was continued for an hour, with heating on a water bath. Subsequent processing of the reaction mixture caused an oily liquid to separate out, which was subjected to ether and then alcohol extraction after removal of the alkaline solution; the alcohol solution was heated with activated charcoal. Driving off of the solvents gave 11.8 g 6-quinolylphenylcarbinol (53%), with m.p. 97-98°. Recrystallization from a small quantity of alcohol with lengthy cooling produced the carbinol in the form of colorless crystals, m.p. 102-103°, readily soluble in the usual organic solvents, very slightly in light gasoline

0.1850 g sub.: 8.32 ml NaOH. Found %: N 5.72. $C_{16}H_{13}ON$. Calculated %: N 5.95.

The picrate, obtained in alcoholic solution and recrystallized from glacial acetic acid, consisted of yellow crystals, m.p. 177-178°.

Effect of alkyl halides on 6-quinolylphenylcarbinol.

a) 0.5 g carbinol and 0.6 g iodomethane were heated in a boiling water bath for an hour. Recrystallization from glacial acetic acid gave 0.72 g (90%) yellow crystalline 6-quinolylphenylcarbinol iodomethylate, m.p. 146-147°. The iodomethylate dissolved in water and alcohol, but not in dry ether.

0.1220 g sub.: 0.0752 g AgI. Found %: I 33.32. $C_{17}H_{16}ONI$ Calculated %: I 33.66.

b) 0.55 g carbinol and 0.6 g bromoethane were heated for 2 hours at 85-90° in a sealed tube. Recrystallization from glacial acetic acid gave 0.48 g (60%) colorless 6-quinolylphenylcarbinol bromoethylate crystals, m.p. 204°. They dissolved in water and alcohol, but not in dry ether.

0.1400 g sub.: 0.0754 g AgBr. Found %: Br 22.93. $C_{18}H_{18}ONBr$. Calculated %: Br 23.22.

Oxidation of 6-quinolylphenylcarbinol. 2 g chromium trioxide was added in 30 minutes, bit by bit, with heating on a boiling water bath, to 5.2 g carbinol dissolved in 20 ml glacial acetic acid; heating at 115° continued for 15 minutes. Subsequent processing gave 2.4 g (46.5%) 6-quinolylphenyl ketone; recrystallization from butyl alcohol produced the ketone as colorless crystals, m.p. 63°. It dissolved readily in the usual organic solvents, but very slightly in gasoline.

0.1362 g sub.: 6.18 ml NaOH. Found %: N 5.77. $C_{16}H_{11}ON$. Calculated %: N 6.01.

The picrate, obtained in alcoholic solution and recrystallized from glacial acetic acid, consisted of yellow crystals, m.p. 219°.

Effect of iodomethane on 6-quinolylphenyl ketone. 0.6 g ketone and 0.7 g iodomethane were heated for 30 minutes on a boiling water bath. Recrystallization from glacial acetic acid gave light-brown crystals, iodomethylate of 6-quinolylphenyl ketone, and m.p. 214-215° (67.7%). They dissolved in water and alcohol, but not in dry ether.

0.1584 g sub.: 0.1000 g AgI Found %: I 34.12. $C_{17}H_{14}ONI$ Calculated %: I 33.84.

6-quinolyldiphenylhydrazone consisted of yellow crystals with m.p. 165-166° (from alcohol).

0.1036 g sub. : 10.29 ml NaOH. Found %: N 12.64. $C_{22}H_{17}N_3$. Calculated %: N 12.92.

Synthesis of 6-quinolyl-α-naphthylcarbinol. 12.2 g aldehyde and 200 ml dry ether were added by drops in 30 minutes, with water cooling, to an ether solution of α-naphthylmagnesium bromide (1.9 g metallic magnesium, 50 ml dry ether, 16.1 g freshly-distilled α-bromonaphthalene) [3]; the reaction was continued for an hour with heating on a water bath. Subsequent processing produced a bright yellow precipitate. Alcohol extraction in an extractor gave 7.6 g (34.3%) 6-quinolyl-α-naphthylcarbinol; recrystallization from a mixture of alcohol and glacial acetic acid produced the carbinol as colorless crystals, b.p. 212°. They were slightly soluble in alcohol, but soluble in glacial acetic acid.

0.1604 g sub.: 5.58 ml NaOH. Found %: N 4.43. $C_{20}H_{15}ON$. Calculated %: N 4.91.

The picrate consisted of yellow crystals, m.p. 177° (from glacial acetic acid).

Effect of alkyl halides on 6-quinolyl-α-naphthylcarbinol.

a) 0.64 g carbinol and 0.62 g iodomethane were heated in a sealed tube for 6 hours at 100-110° (an attempt to heat on a boiling water bath yielded the initial carbinol after two hours). Washing with glacial acetic acid with heating gave 0.9 g (94.7%) yellow crystalline 6-quinolyl-α-naphthylcarbinol iodomethylate, m.p. 240°. It dissolved in water with heating, and, with greater difficulty, in alcohol and glacial acetic acid.

0.1014 g sub.: 0.0558 g AgI Found %: I 29.75. $C_{21}H_{18}ONI$ Calculated %: I 29.71.

b) 0.24 g carbinol and 0.5 g bromoethane were heated in a sealed tube at 100-110° for 12 hours. The initial carbinol, m. p. 212°, was returned; a sample mix melted at the same temperature.

SUMMARY

1. 6-Quinolylmethyl-, ethyl-, phenyl- and α-naphthylcarbinols were synthesized by reacting magnesium halide alkyls and aryls with anhydrous 6-quinolylaldehyde in ether solution. The homologous alkyl halides were obtained by heating the carbinols with iodomethane and bromoethane.

2. 6-Quinolylmethyl, ethyl, and phenyl ketones, identified in the form of iodomethylates and phenylhydrazones, were synthesized by oxidizing 6-quinolylcarbinols with chromium trioxide in glacial acetic acid solution.

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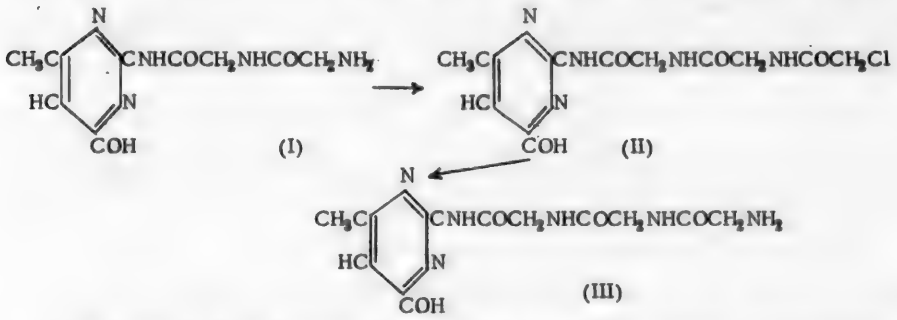
*See Consultants Bureau Translation, page 1785.

SYNTHESIS OF SOME HALOACETYL AND AMINOACETYL DERIVATIVES OF 2-AMINOPYRIMIDINE AND GUANINE

M. A. Prokofyev, Z. A. Shabrova, and E. G. Antonovich

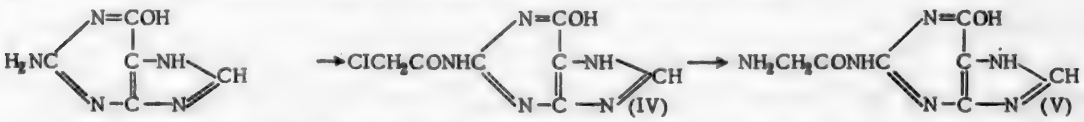
Earlier we had synthesized a number of acyl (acetyl, chloroacetyl, aminoacetyl) derivatives of the 2-aminopyrimidines and had studied the the hydrolytic stability of these compounds [1]. In the present investigation we continued our study of similar derivatives of 2-amino-4-hydroxy-6-aminopyrimidine and of guanine.

The careful reaction of chloroacetyl chloride with 2-glycyglycylamino-4-hydroxy-6-methylpyrimidine (I) in chloroform gave 2-chloroacetyl lycylglycylamino-4-hydroxy-6-methylpyrithidine (II) in excellent yield, the amination of which in liquid ammonia readily gave 2-glycylglycylglycylamino-4-hydroxy-6-methylpyrimidine (III).



The structure of the obtained compounds was proved by hydrolysis. The hydrolysis of (II) with water gave chloroacetylglycylglycine and 2-amino-4-hydroxy-6-methylpyrimidine; the hydrolysis of (III) with concd. HCl gave glycylglycine (as the hydrochloride), glycine (as the hydrochloride of the methyl ester) and 2-amino-6-methylpyrimidine.

In contrast to the 2-aminopyrimidines, the chloroacylation of guanine proceeds with great difficulty. The reaction can be made to proceed with excellent yield in a melt with chloroacetyl chloride, with the addition of a small amount of phosphoric acid. The conversion of 2-chloroacetylamino-4-hydroxypurine (IV) to 2-glycylamino-4-hydroxypurine (V) is accomplished with comparative ease in liquid ammonia.



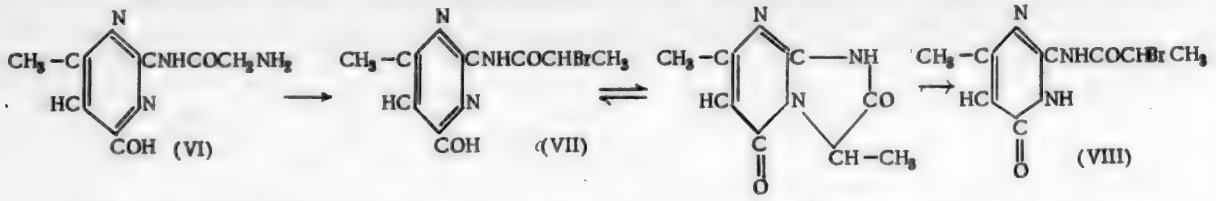
A study of the comparative hydrolytic stability of the amino acylated derivatives of 2-aminopyrimidines reveals that the stability of the amide linkage sharply decreases in the order: acetyl, haloacetyl, and aminoacetyl derivatives. As had been shown by us earlier [1], the acetylamino derivatives of the pyrimidines fail to hydrolyze under prolonged boiling with water; boiling for 2 hours with water is sufficient to cause the decomposition of the chloroacetylamino derivatives, while the aminoacetyl derivatives are completely hydrolyzed even with a short heating period (10-15 minutes). In all cases the amide linkage in the 2-glycylglycylaminopyrimidine is hydrolyzed long before the peptide linkage suffers hydrolysis.

The stability to hydrolysis of the aminoacyl derivatives of 2-aminopyrimidines is increased if the terminal amino group is protected (for example, by phthalation). Thus, 2-phthalylglycylamino-4-chloro-6-methylpyrimidine in its hydrolytic stability approaches 2-chloroacetylamino-4-chloro-6-methylpyrimidine.

The chloroacetylamino derivative of guanine is stable toward boiling water, also (V) is quite stable under these conditions.

In the process of obtaining the polyaminoacyl derivatives of the 2-aminopyrimidines we were able to observe the replacement of the aminoacetyl residue in the corresponding derivative of the 2-aminopyrimidine by the α-bromopropionyl group. When α-bromopropionyl bromide was reacted with 2-glycylamino-4-hydroxy-6-

methylpyrimidine (VI), instead of the expected 2-(α-bromopropionylglycylamino)-4-hydroxy-6-methylpyrimidine we obtained 2-(α-bromopropionylamino)-4-hydroxy-6-methylpyrimidine (VII), while the amination of the latter gave 4-oxo-6-methylpyrimidine-2,3:2', 3'-4-methyldihydroimidazol-5'-one (VIII), as the result of the following reactions:



The obtained pyrimidinoimidazolone derivative was completely identical with the corresponding compound that had been described by us earlier [2].

EXPERIMENTAL

2-Chloroacetylglycylglycylamino-4-hydroxy-6-methylpyrimidine (II). To a solution of 1.7 g of chloroacetyl chloride in 100 ml of dry chloroform was added with rapid stirring 1.2 g of finely ground 2-glycylglycylamino-4-hydroxy-6-methylpyrimidine (I). The vigorous separation of a flocculent precipitate began almost immediately, which was filtered and washed with dry ether. M.p. 156°. Yield 80%.

Found %: N 21.97, 21.85 (Kjeldahl). $C_{11}H_{14}O_4N_5Cl$. Calculated %: N 22.2

The compound was subjected to hydrolysis by boiling it in water for 3 hours. From 0.7 g of (II) after cooling of the hydrolyzate there was obtained 0.25 g of 2-amino-4-hydroxy-6-methylpyrimidine with m.p. 296°. No depression of the melting point was observed when it was mixed with the synthesized product.

Found %: N 33.4 (Kjeldahl). $C_5H_7ON_3$. Calculated %: N 33.6

The filtrate was evaporated to dryness in vacuo and the residue was treated with dry chloroform. The chloroacetyl glycylglycine was separated from the chloroform extract. M.p. 175°, the mixed melting point with the synthesized preparation failed to show a depression.

2-Chloroacetylglycylglycylamino-4-hydroxy-6-methylpyrimidine (II) is completely hydrolyzed under the conditions for the Van Slyke determination of amino nitrogen, in which connection 2 amino groups are determined (one from aminopyrimidine, the other being derived from the hydrolysis of the peptide linkage).

2-Glycylglycylglycylamino-4-hydroxy-6-methylpyrimidine (III). Five grams of finely divided 2-chloroacetylglycylglycylamino-4-hydroxy-6-methylpyrimidine (II) was shaken in an autoclave with 50 ml of liquid ammonia for 6 hours. The ammonia was removed by evaporation and the residue was thoroughly washed with anhydrous methyl alcohol until the precipitate and fresh portions of the filtrate failed to give a reaction for halogen. M.p. 216-218° (with decomposition). Yield 73%.

Found %: N 28.32, 28.50 (Kjeldahl). $C_{11}H_{16}O_4N_6$. Calculated %: N 28.87.

If the usual conditions are used for the Van Slyke determination of amino nitrogen, then 3 amino groups are determined: the terminal amino group, arising in the hydrolysis of the amide linkage, the 2-amino group of the pyrimidine, and the amino group resulting from the hydrolysis of one of the peptide bonds. However, if the product is first boiled for 9 hours with hydrochloric acid (d 1.19), then all 4 possible amino groups are determined.

The compound was subjected to hydrolysis for the purpose of isolating the decomposition products. The substance (2.8 g) was treated with 16 ml of hydrochloric acid (d 1.19) at room temperature for 2.5 hours. The hydrolyzate was evaporated in vacuo to $^1/_3$ of the original volume. The obtained hydrochloride of 2-amino-4-hydroxy-6-methylpyrimidine was filtered, and then by subsequent solution in water and precipitation with 10% NaOH it was converted to the free base. M.p. 294° (from water). The mixed melting point with the synthetic preparation failed to show a depression.

Found %: N 33.12, 33.65 (Kjeldahl). $C_5H_7ON_3$. Calculated %: N 33.6.

The filtrate was evaporated in vacuo to a sirupy consistency, and then was saturated with HCl gas for 2 hours at 0°. The obtained crystalline deposit of glycylglycine hydrochloride was filtered, washed with concd. hydrochloric acid, and thoroughly dried. The compound gives a biuret reaction of the dipeptide type.

Found %: Cl 21.36 (by Volhard). $C_4H_8O_3N_2 \cdot HCl$. Calculated %: Cl 21.05.

To the filtrate was added 5 ml of CH_3OH, saturated in the cold with HCl gas. With strong cooling and stirring the hydrochloride of glycine methyl ester was obtained, m.p. 173°. The mixed melting point of this ester with the synthesized product failed to show a depression.

2-Chloroacetylamino-4-hydroxypurine (IV). To 10 g of chloroacetyl chloride, heated to 90°, was added 2-3 drops of phosphoric acid and gradually with constant stirring there was introduced 3 g of guanine, finely ground in a mortar. The temperature of the melt was maintained at 120-125° for 30 minutes. The reaction mass was transferred to a porcelain mortar and after cooling, was thoroughly rubbed with ether several times (to remove chloroacetic acid and unreacted chloroacetyl chloride). The deposit was filtered and recrystallized from water. M.p. 267-269° (with introduction of the capillary into the block previously heated to 240°). Yield 67%.

Found %: C 36.64; H 2.94; N 30.6; Cl 15.30. $C_7H_6O_2N_5Cl$. Calculated %: C 37.0; H 2.65; N 30.7; Cl 15.4.

The substance is difficultly soluble in alcohol and cold water, more readily soluble in hot water; insoluble in the ordinary organic solvents. Prolonged boiling with water fails to hydrolyze the compound.

2-Glycylamino-4-hydroxypurine (V). Five grams of finely divided dry 2-chloroacetylamino-4-hydroxypurine (IV) was treated with 100 ml of dry liquid ammonia. The mixture was shaken in an autoclave at room temperature for 3 hours. The ammonia was evaporated and the ammonium chloride was removed from the residue by washing with methyl alcohol. The white powder was recrystallized from water. The substance crystallizes as the monohydrate and is infusible up to 400°. Yield 77%. One amino group is determined by the Van Slyke method under normal conditions. The substance is insoluble in the ordinary organic solvents, poorly soluble in cold water and alcohol.

Found %: C 37.61; H 4.40; N 37.00. $C_7H_8O_2N_6 \cdot H_2O$. Calculated %: C 37.17; H 4.42; N 37.17.

2-(α-Bromopropionylamino)-4-hydroxy-6-methylpyrimidine (VII). To 35 g of α-bromopropionyl bromide in 130 ml of dry chloroform was added 10.7 g of 2-glycylamino-4-hydroxy-6-methylpyrimidine (VI). The reaction was run at 75-80° for 5 hours. The chloroform was removed in vacuo. The substance was recrystallized from methyl alcohol, m.p. 170°; completely analogous to thepreparation described by us earlier [2].

Found %: C 37.4; H 4.07; N 16.10. $C_8H_{10}O_2N_3Cl$. Calculated %: C 36.92; H 3.87; N 16.15.

4-Oxo-6-methylpyrimidino-2,3:2',3'-4-methyldihydroimidazol-5'-one (VIII). Two grams of 2-(α-bromopropionylamino)-4-hydroxy-6-methylpyrimidine (VII) was treated with 40 ml of liquid ammonia. The solution was allowed to stand for several days in a sealed glass ampule. The residue, remaining after removal of the ammonia, was recrystallized from water. M.p. 282° (with decomposition). The substance is analogous to the product described by us earlier [2].

Found %: C 53.12; H 5.09; N 23.29. $C_8H_9O_2N_5$. Calculated %: C 53.63; H 5.03; N 23.46.

SUMMARY

1. A method was developed for the preparation of mono-, di-and triaminoacyl derivatives at the amino group of 2-amino-pyrimidines and of guanine by the method of reacting the latter compounds with α-haloaliphatic acid halides, followed by amination. The comparative hydrolytic stability of the obtained compounds was studied.

2. In some cases it was observed that overacylation occurs in the reaction of α-bromoaliphatic acid bromides with the aminoacyl derivatives of 2-aminopyrimidines. An example of such a reaction is to be found in the formation of 2-(α-bromopropionylamino)-4-hydroxy-6-methylpyrimidine from 2-glycylamino-4-hydroxy-6-methylpyrimidine under the influence of α-bromopropionyl bromide.

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Moscow State University

ABSORPTION SPECTRA AND FINE STRUCTURE OF THE SUBSTITUTION DERIVATIVES OF QUINOLINE, THE INITIAL SUBSTANCES FOR ANTIMALARIALS

II. TAUTOMERISM OF THE 2-AND 4-METHYLPYRIDINES*

V. I. Bliznyulkov and V. M. Reznikov

The chemical properties of 2- and 4-amino- and methylpyridine, and of pyridone differ sharply from the corresponding third position substitution derivatives. Subsequent to the studies of Chichibabin [1], the opinion that the specific peculiarities of these compounds reflect tautomerism became deeply rooted in the literature. However, data contradicting the tautomerism of 2-aminopyridine was discovered by Goldfarb [2], and Anderson did likewise for 4-aminopyridine [23]. As one of us had demonstrated by detailed spectrographic analysis in the ultraviolet that no tautomerism actually exists in 2- and 4-aminopyridine [3], and as this was later confirmed in other studies [21,22] it appeared to us to be of interest to extend this research to methylpyridine and pyridone.

The present study is devoted to the absorption spectra of pyridine and 2- and 4-methylpyridine. Analysis of the absorption spectra of pyridine and its derivatives was based on the principles established by Valashko [4] in his studies of benzene derivative spectra. He demonstrated that introduction of such electron acceptor groups as the nitro and aldehyde groups, etc., into the benzene molecule resulted in the appearance of two absorption bands in the middle ultraviolet ("α-type" spectrum). The presence of such electron donor groups in the benzene molecule as the hydroxyl or the amino resulted in the appearance of a single absorption band (the "φ-type"). Accumulation of a number of electron acceptor groups (dialdehyde, nitroaldehyde) in the benzene ring is characterized by a rise in the intensity of absorption and a slight bathochromic shift in the curve, but the α-type spectrum remains unchanged. Accumulation of a number of electron donor groups in the ring (diamines, diatomic phenols, etc.) also raises the intensity of absorption, but the phenol-type absorption spectrum remains. Presence of both types of substitutes in ortho position within the benzene molecule results in an α-spectrum (or "ortho type") with two absorption bands of high intensity. When the substitutes are in the para position the resultant " para bands" intensify phenol type spectra with a single high intensity absorption band ("para type" spectrum) in the middle ultraviolet.

Pyridine Absorption Spectra

The absorption spectra of pyridine in the ultraviolet have been studied repeatedly and with the use of various solvents. First Hartley discovered one broad band with a maximum at λ 2530 A[5]. This same band was found by other investigators [6,24]. Fischer and Steiner [7] found on one side of the main band in hexane a group of five narrow bands that merged in water and ethanol. Finally, it was determined that the main band, too (2530 A), has a fine structure and consists of three narrow bands [8]. On the basis of external similarities, some authors regard the pyridine spectrum as identical with that of benzene [7]. Sponer and Stuklen [9], analyzing the absorption spectrum of pyridine vapor and examining the main elements of symmetry of pyridine and benzene, found that the absorption spectrum of pyridine has a greater similarity to that of substituted benzenes than to that of benzene itself.

However, the fact must be taken into consideration that in analyzing absorption spectra it is inadequate to limit oneself to the molecule's elements of symmetry, as an important role is also played by the nature of the substituents, whose interaction with the π-electrons in the ring is responsible for the optical properties of the molecule's electron shell. With the same symmetry, but with substitutes of varying nature (whether electron donor or electron acceptor), a molecule will have sharply different absorption spectra. This is expressed in Valyashko's principles for the benzene series described above.

In the middle ultraviolet, pyridine has two bands (Fig. 1, curve 1) characteristic of "α-type" spectra and its absorption spectrum calls to mind those of nitrobenzene or benzaldehyde, while in intensity, too, its bands resemble those of nitrobenzene more than benzene proper. Comparison of pyridine and nitrobenzene will show not only identity of elements of symmetry but also very close similarity in the structure, position and intensity of the spectral bands. Measurements are adduced below in confirmation of this. Table 1 compares the position and intensity of the absorption bands of pyridine, benzene and nitrobenzene.

* A brief communication drawn from V. M. Reznikov's dissertation for the degree of Candidate.

TABLE 1*

No.	Name	Low intensity band spectrum			Main band maximum		
		λ (A)	ε	ε: ε nitrobenzene	λ (A)	ε	ε: ε nitrobenzene
1	Pyridine (from ε100 to, ε2000, according to Fischer and Steiner) in hexane	2810	640	1 : 1,2	2520	2090	1 : 2
2	Benzene (according to Fischer and Steiner) in hexane	2680	8	1:100	2550	200	1:20
3	Nitrobenzene (according to Valyashko) in hexane	2800	790	1	2520	4270	1

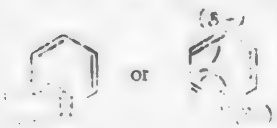
* In Table 1, the position of the absorption maximum of the main benzene band, and of the low intensity pyridine band represent arithmetical means of the positions of the absorption maxima of the respective group of bands.

Comparison of the absorption curves of pyridine, benzene and nitrobenzene, as presented in Fig. 1 and Table 1, shows that the first main absorption band (Fig. 1, curves 1,4,5) which lies at λ_{max} 2500-2520 A in all three cases, is, for pyridine, 10 times as intense as for benzene, but no more than half as intense as for nitrobenzene. An even greater difference will be noted between the positions of the low intensity bands of benzene and pyridine, and, conversely, similarity between pyridine and nitrobenzene. With benzene this band is only 1/100th as intense and is shifted 120 A toward the shorter wave side, while it is identical in intensity for nitrobenzene and pyridine and lies in the same wavelength area.

Thus, comparison of the absorption spectra of benzene, pyridine and nitrobenzene testifies to the fact that ring nitrogen is optically similar to the nitro and aldehyde groups.

Chichibabin was apparently the first to note the similarity of ring nitrogen and the nitro group [10], while Sidgwick [11] and, particularly, Mosher [12] later developed this thought in detail.

Ring nitrogen (an electron acceptor substitute), reacting with the π-electrons of the ring, deforms the electron system of the pyridine molecule so as to create some degree of positive charge at the 2- and 4-positions.



Accordingly, absorption bands appear in the spectra similar to those in the spectra of nitrobenzene or benzaldehyde. As a result, the intensity of the main pyridine absorption band rises 10-fold by comparison to that of benzene. In dipole solvents such as water, ethanol, and chloroform, able to bond the "noncovalent" electron pair of ring nitrogen, pyridine acts as a weak base and is capable of forming unstable addition products. A system in equilibrium is established in the solution.

$$C_5H_5N + HOH \rightleftharpoons C_5H_5N - HOH \rightleftharpoons [C_5H_5NH]^+ OH^-.$$

In the instance given above, the formation of the pyridine cation is accompanied by a 70% rise in absorption intensity relative to that in nondipole hexane (Fig. 1, curves 2,3).

With acids pyridine forms a salt:

$$C_5H_5N \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [C_5H_5NH]^+$$

The concentration of the pyridine cation rises, and parallel thereto the intensity of the main band increases 2 1/2-fold relative to absorption in hexane, and by 40% relative to absorption in water and in ethanol (Fig. 2, curves 2,3).

The process of salt formation is apparently consummated at a 1:1 molar ratio between pyridine and acid, as no further change in intensity is observed in concentrated 98% sulfuric acid. Measurement data are presented in Table 2.

Examination of the absorption spectra and chemical properties of pyridine indicates the dual nature of ring nitrogen: when it gains electrons, it behaves like an electron acceptor substituent; when it loses them, it is capable of forming ammonia salts.

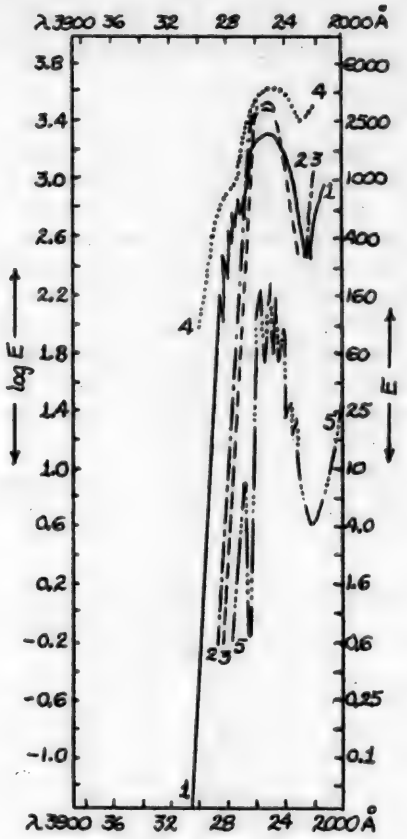


Fig. 1. 1) Pyridine in hexane from 2 to $2 \cdot 10^{-4}$ mole (from ε100 to ε2000, according to Fischer and Steiner); 2) pyridine in ethanol from $2 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ mole; 3) same, in water; 4) nitrobenzene in hexane, according to Valyashko (partial curve); 5) benzene in hexane, according to Fischer and Steiner.

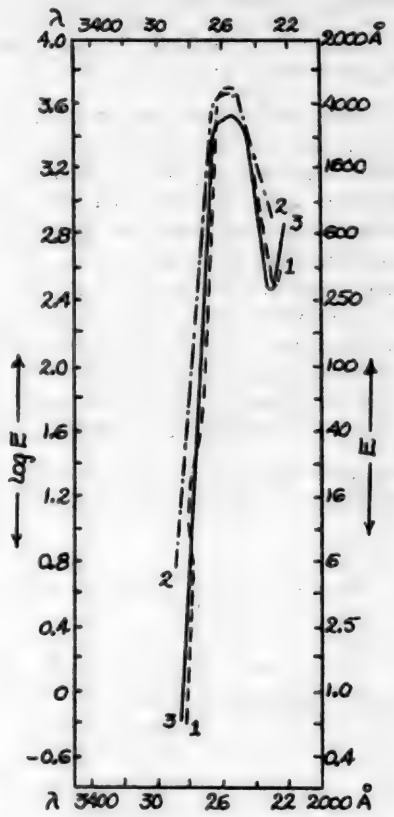


Fig. 2. 1) Pyridine in 16.5 mole sulfuric acid from $2 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ mole; 2) pyridine in ethanol (1:1 mole HCl) from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 3) pyridine in ethanol.

TABLE 2

No.	Name	Main band maximum		ε (in hexane): ε (in solvent).
		λ (A)	ε	
1	Pyridine in hexane	2520	2090	
2	Pyridine in water	2530	3600	1 : 1.7
3	Pyridine in ethanol	2530	3600	1 : 1.7
4	Pyridine in an ethanol solution of hydrogen chloride (1 : 1)	2545	5200	1 : 2.5
5	Pyridine in concentrated 98% sulfuric acid . . .	2525	5200	1 : 2.5

4-Methylpyridine Absorption Spectra

The absorption spectra of 4-methylpyridine in aqueous solutions were investigated first by Herington [13] and then by Daeniker [14]. They found a single broad band of fine structure.

We studied the absorption spectra of 4-methylpyridine in hexane, water, ethanol, chloroform, sodium ethylate,

hydrogen chloride in ethanol solution, and in concentrated 98% sulfuric acid. Absorption spectra in all these solvents were studied in the concentration interval from $2 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ moles. 4-Methylpyridine dissolved in $2 \cdot 10^{-}$ mole concentration of hexane only when heated.

Within this interval of concentration in hexane, a single wide band with maximum at λ 2620 A and ϵ 2000 was found (Fig. 3, curve 1).

Comparison of the absorption spectra curve of 4-methylpyridine and p-nitrotoluene in hexane (Fig. 3, curves 1,5) shows close similarity. This is explainable not by equivalence of ring nitrogen and the nitro group, but by similarity in their electron acceptor effect upon the electron system of the ring. The absorption maxima of the main band lie at the same wavelength and differ only in intensity. When a methyl group is introduced into the pyridine molecule abathochromic shift results, similar to that occurring during the transition from nitrobenzene to p-nitrotoluene. This is explained by the fact that a σ, π-conjugate is established between the methyl and nitro groups in the p-nitrotoluene molecule, and between the ring nitrogen and the methyl group in the 4-methylpyridine molecule, loosening the electron system of the molecule and thereby requiring less energy for excitation. In acids and in solvents (water, ethanol, chloroform) capable of bonding the "noncovalent" electron pair of nitrogen, the intensity of the main absorption band rises 50 to 150% and in acids the curve is also displaced somewhat toward the longer wavelengths (Fig. 3, curves 3,4,7,8), but the pyridine type of absorption is not changed. Table 3 presents measurements characterizing 4-methylpyridine absorption maxima positions in various solvents.

As with pyridine, the rise in absorption intensity of the main 4-methylpyridine band in ethanol, water, chloroform and acids relative to absorption in hexane is explained by the formation of the pyridine cation.

TABLE 3

No.	Name	Main band max.		ϵ (in hexane): ϵ (in solvent)
		λ (A)	ϵ	
1	4-Methylpyridine in hexane	2615	2000	1 : 1
2	" " water	2600	3200	1 : 1.5
3	" " ethanol	2620	3200	1 : 1.5
4	" " sodium ethylate	2620	3200	1 : 1.5
5	" " chloroform	2620	4100	1 : 2.1
6	" " 1:1 HCl ethanol solution	2615	5200	1 : 2.5
7	" " 16.5 mole sulfuric acid	2605	5200	1 : 2.5

TABLE 4

No.	Name	Main band max.		ϵ (in hexane): ϵ (in solvent)
		λ (A)	ϵ	
1	2-Methylpyridine in hexane	2600	2000	
2	" " water	2600	4000	1 : 2.0
3	" " chloroform	2630	4500	1 : 2.2
4	" " ethanol	2600	4000	1 : 2.0
5	" " sodium ethylate	2600	4000	1 : 2.0
6	" " 1:1 HCl ethanol solution	2620	5200	1 : 2.6
7	" " 98 % sulfuric acid	2605	5200	1 : 2.6

2-Methylpyridine Absorption Spectra

2-Methylpyridine had been the object of spectrographic research by several authors [5, 6, 15], who found one absorption band with λ_{max} 2610 A. It was shown later that this band was of fine structure [13, 14].

We studied the absorption spectra of 2-methylpyridine in hexane, water, chloroform, sodium ethylate solution, hydrogen chloride in ethanol solution (1 : 1 molar ratio of 2-methylpyridine and HCl), and in concentrated 98% sulfuric acid.

In all solvents except hexane, 2-methylpyridine was studied in concentration intervals from $2 \cdot 10^{-1}$ to

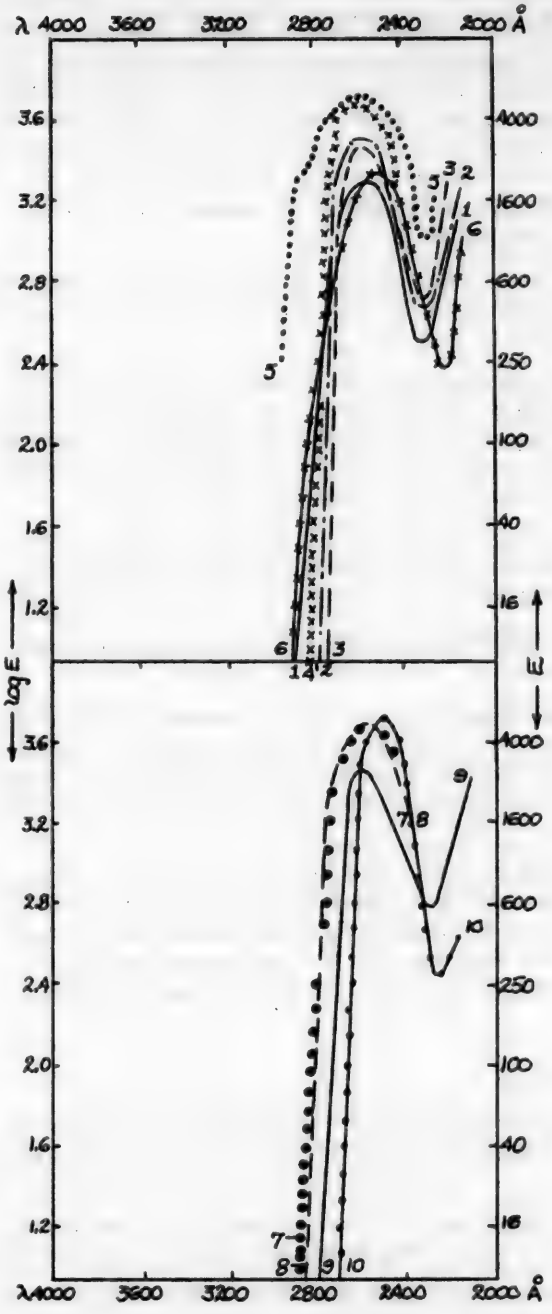


Fig. 3. 1) 4-Methylpyridine in hexane from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 2) same, in ethanol; 3) same, in water; 4) same, in chloroform; 5) p-nitrotoluene in hexane, according to Valyashko (parial curve); 6) pyridine in hexane; 7) 4-methylpyridine in ethanol (1:1 mole HCl) from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 8) same in 16.5 mole sulfuric acid from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 9) same in ethanol; 10) pyridine in 16.5 mole sulfuric acid.

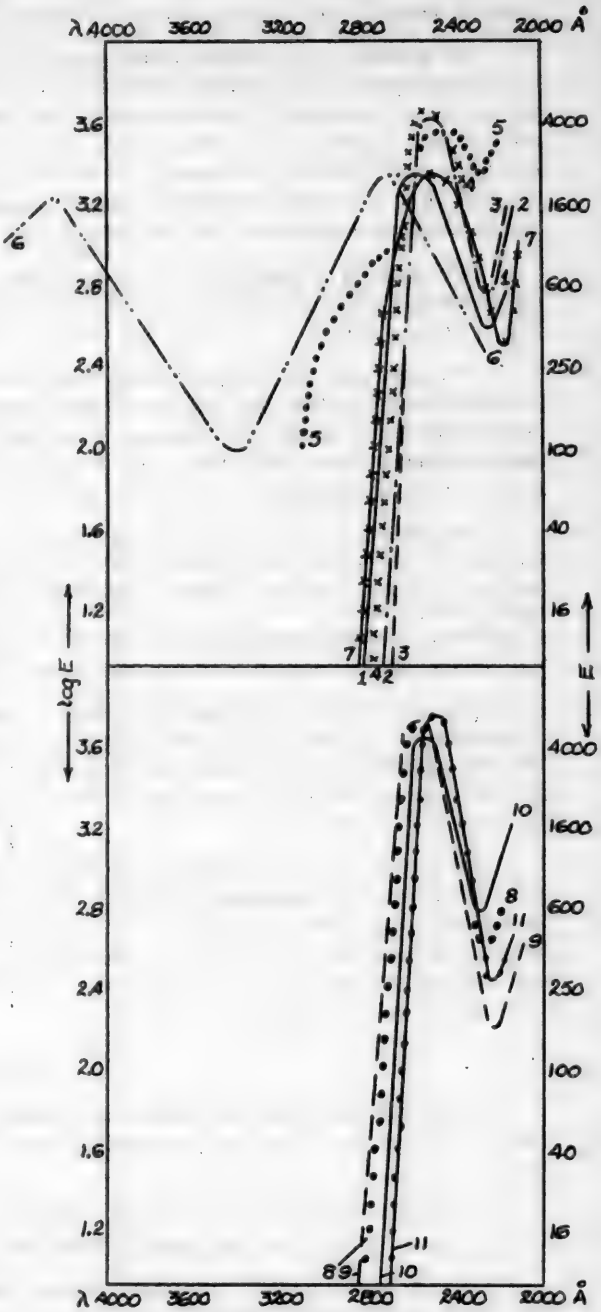


Fig. 4. 1) 2-Methylpyridine in hexane from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 2) same, in ethanol; 3) same, in water; 4) same, in chloroform; 5) o-nitrotoluene in hexane according to Valyashko (partial curve); 6) 1-methyl-2-methylenedihydropyridine in ether, according to Anderson and Seeger; 7) pyridine in hexane; 8) 2-methylpyridine in ethanol (1:1 mole HCl) from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ mole; 9) same in 16.5 mole sulfuric acid; 10) 2-methylpyridine in ethanol; 11) pyridine in 16.5 mole sulfuric acid.

$2 \cdot 10^{-4}$ mole. One band was found with λ_{max} 2600 A. In hexane, 2-methylpyridine was studied from the liquid to $2 \cdot 10^{-4}$ mole. In this concentration interval also, one band was found at λ_{max} 2600 A. Table 4 presents the positions of the maxima and the intensity of the main 2-methylpyridine absorption band.

Fig. 4 presents curves for the absorption spectra of 2-methylpyridine in neutral solvents (curves 1,2,3,4) and in acids (curves 8,9) (the absorption of 2-methylpyridine in sodium ethylate is the same as in ethanol, and therefore no curve is presented). The measurement data presented in Fig. 4 and Table 4 testify to the fact that in acid solutions and in polar solvents such as water, ethanol, and chloroform, the absorption intensity of 2-methylpyridine rises 100 to 150% relative to its absorption in hexane. As in the previous instances, this increase in intensity is explained by the bonding of the ring nitrogen " noncovalent" electron pair by the molecules of the solvent, and by increased conjugation of the ring nitrogen with the methyl group.

The character of the effect of σ, π-conjugation in the 2-methylpryidine molecule recalls the conjugation of the methyl and nitro groups in the 2-nitrotoluene molecule, testifying to the optical similarity of these compounds (Fig. 4, curves 1 and 5).

Thus, spectrographic study of pyridine and 2- and 4-methylpyridine solutions in neutral, acid and basic solvents demonstrates that their absorption spectra belong to the pyridine type and resemble those of the corresponding nitro derivatives of the benzene series. Absorption bands characteristic of the methylenedihydropyridine tautomer were not observed in any of the three types of solvents, a fact most evident upon comparison of the 2-methylpyridine spectrum with the absorption spectrum of 1-methyl-2-methylenedihydropyridine (Fig. 4, curves 1,7).

The pyridine structure of 2- and 4-methylpyridine is also confirmed by their infrared and Raman spectra. The infrared spectra of 2-(and 3-methylpyridines are known to be identical, and 3-methylpyridine is structurally incapable of tautomerism. The Raman spectra of all three methylpyridines reveal [16] a bright line at ν 990 cm^{-1}, identical with that of toluene, xylol and mesitylene.

Finally, measurements of the parachor, molecular refractivity and dipole moments [18] confirm the fact that the methylpyridines exist only in pyridine form.

The dual reactivity of the methylpyridines is a consequence of σ, π-conjugation and not of tautomerism. Depending upon the conditions of reaction and the effect of the active agent, the center of reaction is transferred from the ring nitrogen to the methyl group and vice versa. This view is substantiated by the fact that the methyl group in quaternary ammonia compounds of methylpyridine has greater reactivity than in the free base, yet tautomerism is out of the question here.

The pyridine, 2-, and 4-methylpyridine used in the spectrographic research were purified by means of oxalates [19]. The purity of the preparations was verified by the melting points of the picrates: pyridine 166°, 2-methylpyridine 163°, and 4-methylpyridine 164°. The literature [20] shows the picrate melting points to be 167° for pyridine, 163-164° for 2-methylpyridine, and 165-167° for 4-methylpyridine. The spectra were photographed with a Hilger quartz spectrograph. The source of light was a spark across ferrotungsten electrodes, giving a spectrum from the visible to 2000 Å.

SUMMARY

1. The ultraviolet absorption spectra of pyridine, 4-methylpyridine and 2-methylpyridine were studied in hexane, water, ethanol, chloroform, an ethanol solution of hydrogen chloride, 98% sulfuric acid and sodium ethylate.

2. The dual character of ring nitrogen, expressed in the attraction of electrons from the pyridine ring (similarly to the nitro group) and the yielding of electrons, with the formation of ammonia-type salts, was demonstrated.

3. It was postulated that the increased intensity and bathochromic displacement of the main absorption band of 2- and 4-methylpyridine relative to pyridine was caused by the σ, π-conjugation of ring nitrogen with the methyl group, and an explanation of their dual reactivity was offered in terms of the concept of transfer of center of reaction.

4. The ultraviolet absorption spectra of 2- and 4-methylpyridine do not confirm the concept of their tautomerism.

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*See Consultants Bureau Translation, p. 1253.

INVESTIGATIONS IN THE ANTHRAQUINONE SERIES

XXI. THE HYDROLYSIS OF α-ANTHRAQUINONYLMERCURY CHLORIDE*

V. V. Kozlov and B. I. Belov

As had been shown by one of us [1], the reaction for the sulfonation of anthraquinone to the α-sulfonic acid, using the method of M. A. Ilyinsky [2], in the presence of mercury salts, proceeds in two stages – mercuration of the anthraquinone and sulfonation of the mercury compound.

It had also been shown [3] that the desulfonation or hydrolysis of anthraquinone-α-sulfonic acid, realized in the presence of mercury salts, also proceeds through the formation of the intermediate mercury-containing anthraquinone compound.

In this communication we present the results of our studies on the hydrolysis of the α-mercury-containing anthraquinone compound. For this we first of all took α-anthraquinonylmercury chloride, being the starting product for the synthesis of α-anthraquinonylmercury sulfate [4], the formation of which was predicted from the schemes for the synthesis and hydrolysis of anthraquinone-α-sulfonic acid. The properties of α-anthraquinonylmercury chloride, first obtained by Coppens [5], have to a certain degree been described in our earlier papers, but the behavior of this compound toward hydrolysis is presented by us for the first time.

We realized the synthesis of α-anthraquinonylmercury chloride by the method of A. N. Nesmeyanov, a method that we had tried earlier [4]. In contrast to the earlier experiments on the conversion of the α-anthraquinonediazonium chloride-mercuric chloride adduct to α-anthraquinonylmercury chloride – $RN_2Cl \cdot HgCl_2 \rightarrow$ $\rightarrow$ RHgCl, we studied the transformation of the mercuric chloride adducts of α-anthraquinonediazonium nitrate and acid sulfate ($RN_2SO_4H \cdot HgCl_2$ and $RN_2NO_3 \cdot HgCl_2$).

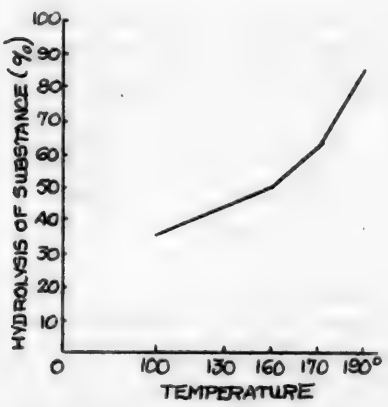

Fig. 1. Hydrolysis of RHgCl as a function of the temperature (0.1 g RHgCl, 10 ml 75% H_2SO_4, 1 hour).

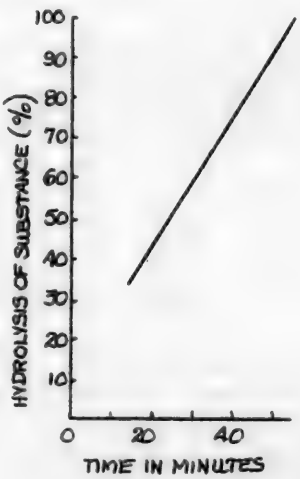

Fig. 2. Hydrolysis of RHgCl as a function of the time (190°, 10 ml 75% H_2SO_4).

According to Nesmeyanov, it was established that the diazo salt anion fails to possess any significance for the formation of the organomercury compound. Mercury, combining with the carbon of the anthraquinone ring, is always attached to the same anion with which it was bound in the binary salt of the original diazo compound, in accord with the scheme:

* For Communication XX, see "Communications of Members of the D. I. Mendeleev All-Union Chemical Society," No. 4, 5 (1950).

$$RN_2X \cdot HgCl_2 \rightarrow RHgCl.$$

The hydrolysis results for α-anthraquinonylmercury chloride are shown in Figs. 1-2 and Tables 1-4. First of all, these results show that the hydrolysis depends on the temperature. Our experiments permitted us to establish that both at 170-175° and at 190-195° the most complete hydrolysis is obtained in 75% sulfuric acid. The original substance itself forms a homogeneous solution only in 75% sulfuric acid and higher. Hydrolysis in more dilute sulfuric acid emphasizes the relative stability of α-anthraquinonylmercury chloride. The small amount of decomposition (5% conversion) obtained when the substance is heated for 1 hour in sulfuric acid monohydrate

TABLE 1

Hydrolysis of RHgCl as a Function of Sulfuric Acid Concentration

Expt. No.	H_2SO_4 (in %)	RHgCl (in g)	KI for 1 ml of solution (in ml)	Mercury found (in g)	Hydrolyzed substance (%)
a) 190-195°; 1 hour; 10 ml H_2SO_4; T_{KI} 0.002295 g Hg					
1	25	0.0991	0.09	0.0207	5.2
2	40	0.1291	0.11	0.0252	49
3	50	0.1493	0.16	0.0367	62
4	60	0.1137	0.13	0.0298	66
5	75	0.1262	0.19	0.0436	96
6	80	0.1140	0.14	0.0321	70.5
7	100	0.0898	0.08	0.0184	5.1
b) 170-175°; 1 hour, 10 ml H_2SO_4; T_{KI} 0.002295 g Hg					
8	40	0.0919	0.08	0.0184	4.9
9	50	0.1185	0.11	0.0252	54.0
10	75	0.1107	0.12	0.0275	62.5
11	85	0.1015	0.105	0.0231	59.4
12	100	0.0747	0.07	0.0161	5.4

TABLE 2

Hydrolysis of RHgCl. Influence of Mercury Sulfate Addition

Expt. No.	H_2SO_4 (in %)	RHgCl (in g)	$HgSO_4$ (in g)	KI for 1 ml of solution (in ml)	Mercury found (in g)	Hydrolyzed substance (%)
190-195°; 1 hour; 10 ml H_2SO_4; T_{KI} 0.002295 g Hg						
1	50	0.1493	–	0.16	0.0367	62
2	50	0.1189	0.0099	0.11	0.0252*	38.5
3	75	0.1262	–	0.19	0.0436	96
4	75	0.0926	0.0099	0.13	0.0298*	62.5

indicates the considerable stability of the substance in anhydrous sulfuric acid. This stability to concentrated acids explains the fact observed by us earlier of the possible conversion of α-anthraquinonylmercury chloride to α-anthraquinonylmercury acid sulfate under the influence of sulfuric anhydride in oleum [4]. The results for the hydrolysis of RHgCl, conducted with the addition of mercury sulfate, up to 10% of the total amount of substance being hydrolyzed, to the reaction mixture, shows that the mercury sulfate hinders the hydrolysis somewhat (Table 2).

The hydrolysis of RHgCl in aqueous sulfuric acid can be depicted as a process composed of the following reactions:

a) $2RHgCl + 2HOH \rightarrow 2HR + 2Hg(OH)Cl,$

b) $2Hg(OH)Cl + H_2SO_4 \rightarrow HgSO_4 + HgCl_2 + HOH,$

c) $RH + HgSO_4 \rightarrow RHgSO_4H,$

d) $RHgSO_4H + HOH \rightarrow RH + HOHgSO_4H.$

$$2HRgCl + 2HOH + H_2SO_4 \rightarrow 2RH + HgCl_2 + HOHgSO_4H.$$

* After subtracting the introduced mercury sulfate.

To the degree that the mercury sulfate formed according to scheme (b) is capable, under the influence of the water contained in the aqueous sulfuric acid, of forming the hydrated amphoteric mercury compound [3]

$$HgSO_4 + HOH \rightarrow HOHgSO_4H,$$

to that degree will the hydrolysis of RHgCl or $RHgSO_4H$ prevail over the possible mercuration reaction. The direct introduction of mercury sulfate into the reaction mixture, i.e., an increase in the concentration of the mercuration agent, already causes a noticeable retardation of the hydrolysis reaction (Table 3).

TABLE 3

Hydrolysis of RHgCl. Influence of Mercury Sulfate Addition in the Hydrolysis Process

Expt. No.	Heating time (in mins)	RHgCl (in g)	$HgSO_4$ (in g)	KI for 1 ml of solution (in ml)	Mercury found (in g)	Hydrolyzed substance (%)
			170-175°; 10 ml 75% H_2SO_4; 6.5% $HgSO_4$; T_{KI} 0.001687 g Hg			
1	30	0.0984	–	0.11	0.0186	47.1
2	30 + 60	0.1115	0.0099	0.13	0.0153*	34.4

TABLE 4

Hydrolysis of RHgCl. Influence of Chlorosulfonic Acid Addition

Expt. No.	RHgCl (in g)	Time (in mins)	KI for 1 ml of solution (in ml)	Mercury found (in g)	Hydrolyzed substance (%)	Remarks
			170-175°; 10 ml 75% H_2SO_4; 10% SO_3HCl; T_{KI} 0.001687 g Hg			
1	0.1107	60	0.16	0.0275	62.5	without SO_3HCl
2	0.1103	60	0.18	0.0304	69.0	with SO_3HCl
3	0.1181	90	0.24	0.0405	86.0	with SO_3HCl
4	0.1098	30	0.17	0.0287	65.3	with SO_3HCl

The possibility of some mercuration of anthraquinone by mercury sulfate in 75% sulfuric acid at 190° was confirmed by us in a separate experiment.

The introduction into the reaction mass (during the time of heating in 75% sulfuric acid at 170-175°) of up to 10% of chlorosulfonic or hydrochloric acid accelerates the hydrolysis process somewhat, especially in the early part of the reaction (Table 4). The value of chlorosulfonic acid or of the chloride ion in general for retarding the mercuration process had been studied by us earlier [7].

The hydrolysis of RHgCl in aqueous sulfuric acid with the addition of SO_3HCl (or HCl) can be depicted as a process that is composed of the following reactions:

$$SO_3HCl + HOH \rightarrow H_2SO_4 + HCl,$$

$$HOHgSO_4H + 2HCl \rightarrow HgCl_2 + HOH + H_2SO_4,$$

$$Hg(OH)Cl + HCl \rightarrow HgCl_2 + HOH,$$

$$HgSO_4 + 2HCl \rightarrow HgCl_2 + H_2SO_4.$$

The mercuric chloride that is formed gradually distills from the reaction mass, in that way making even less possible the mercuration of anthraquinone, proceeding concurrently with the hydrolysis reaction, than when the RHgCl is directly hydrolyzed without the introduction of SO_3HCl or HCl.

EXPERIMENTAL

1. Preparation of α-anthraquinonediazonium double salts. The α-anthraquinonediazonium chloride-mercuric chloride adduct was prepared by the diazotization of α-aminoanthraquinone and subsequent precipitation with mercuric chloride by the earlier described method [4].

To prepare α-anthraquinonediazonium acid sulfate the α-aminoanthraquinone was diazotized, according to Maki [8], in sulfuric acid suspension with dry nitrite. To prepare α-anthraquinonediazonium nitrate 2 g of

* After subtracting the introduced mercury sulfate.

α-aminoanthraquinone was diazotized in 20 ml of nitric acid (d 1.4) at 0-5° with dry nitrite, with stirring for 1.5 hours. After this the mixture was kept for 20 hours at 0-5°, then poured into 200 ml of cold water and suction filtered from unreacted aminoanthraquinone (0.4 g, or 20%). In all three cases of diazotization the obtained diazo solutions couple well with different azo-components.

To each of the obtained diazo solutions (200 ml) was added with vigorous stirring a solution of 6 g of yellow mercury oxide in 50 ml of 15% hydrochloric acid. Heavy crystalline precipitates are obtained, which were filtered, washed with cold water and alcohol, and dried in a darkened desiccator over potassium hydroxide.

Below are given the properties of the α-anthraquinonediazonium salt-mercuric chloride adducts.

Composition	Crystal form	Color	Decomposition point [6]
$RN_2Cl \cdot HgCl_2$	Fine silky needles	Pale yellow	164°
$RN_2SO_4H \cdot HgCl_2$	Stout needles	Yellow	154
$RN_2NO_3 \cdot HgCl_2$	Fine needles	Yellow	152

The dried products couple well with different azo-components. The yields of the different mercuric chloride adducts are as follows: 3.7 g for α-anthraquinonediazonium chloride, 2.2 g for α-anthraquinonediazonium acid sulfate, 3.1 g for α-anthraquinonediazonium nitrate. Analysis of the α-anthraquinonediazonium chloride-mercuric chloride adduct had been made earlier. Analysis of the other diazo salts by decomposition in 80% sulfuric acid with potassium dichromate, with collection of the evolved diazo nitrogen in a Lunge nitrometer over potassium hydroxide, gave the following results:

0.4914 g sub.: 21.9 ml N_2 (20°, 749 mm). Found %: N 5.07. $C_{14}H_7O_2N_2SO_4H \cdot HgCl_2$. Calculated %: N 4.64. 0.4822 g sub.: 21.6 ml N_2 (20°, 750 mm). Found %: N 5.01. $C_{14}H_7O_2N_2NO_3 \cdot HgCl_2$. Calculated %: N 4.95.

Analysis for mercury (by Koshkin [9]). The substance (0.7339 g), after decomposition with sulfuric acid, was dissolved in 300 ml of water. For the titration of 1 ml of this solution there was required 0.69 ml of 0.01 N KI (T = 0.001191 g Hg).

Found %: Hg 33.61. $C_{14}H_7O_2N_2SO_4H \cdot HgCl_2$. Calculated %: Hg 33.2. 0.2122 g substance, after decomposition with sulfuric acid, was dissolved in 100 ml water. The titration of 1 ml of this solution required 0.62 ml of 0.01 N KI. Found %: Hg 34.96. $C_{14}H_7O_2N_2NO_3 \cdot HgCl_2$. Calculated %: Hg 35.21.

Analysis for Chlorine (Volhard): the adduct sample, suspended in water, is coupled for 3 hours with β-naphthol. After standing for a day, the dye is filtered and washed. The mother liquor and wash waters are made up to a volume of 300 ml.

0.5037 g sub.: 1 ml of solution required 0.32 ml of $AgNO_3$ (T = 0.002862). Found % Cl 11.39. $C_{14}H_7O_2N_2SO_4H \cdot HgCl_2$. Calculated %: Cl 11.77. 0.3021 g sub.: 1 ml of solution required 0.42 ml of $AgNO_3$. Found %: Cl 12.21. $C_{14}H_7O_2N_2NO_3 \cdot HgCl_2$. Calculated %: Cl 12.5

Preparation of α-anthraquinonylmercury chloride. One gram of the dry adduct (chloride, acid sulfate or nitrate) was suspended in 30 ml of dry acetone in a beaker with stirring and external cooling. To the suspension was gradually added 0.3 g of copper bronze. The reaction temperature was kept below 25-30°, the decomposition time for the diazo compound was 15 hours. The dark grey or dark brown mass was separated from acetone by filtration, washed on the filter with acetone, and then with hot alcohol. α-Chloroanthraquinone is isolated from the latter solutions in a yield of 0.23-0.17 g (53.5-41%) for the different diazo compounds. The residue on the filter, freed of α-chloroanthraquinone, was washed with 5% ammonia to colorless filtrate, then with water and alcohol, and finally dried at 100°. Yield 0.4-0.58 g (43-59%) from the different diazo compounds, based on α-anthraquinonylmercury chloride.

The substance crystallizes from hot phenol as a bright yellow microscopic powder, having the same composition for all of the original diazo compounds.

Analysis for mercury (by Koshkin): 0.5766 g of substance, after decomposition with sulfuric acid, was dissolved in 300 ml of water. The titration of 1 ml of the solution required 0.72 ml of 0.01 N KI (T = 0.001191 g Hg).

Found %: Hg 44.31. $C_{14}H_7O_2HgCl$. Calculated %: Hg 45.24.

3. Hydrolysis of α-anthraquinonylmercury chloride. The hydrolysis was performed with 0.0002-0.0003 mole of substance, i.e., with 0.1-0.15 g, in small flasks fitted with reflux condensers, in a common oil bath for several samples. During hydrolysis the separation of a product is observed (sublimation and condensation in the neck of the flask), which product gives all of the specific reactions for anthraquinone and mercuric chloride.

After hydrolysis the reaction mass is poured on ice and filtered from anthraquinone and from unreacted starting material. Not even traces of hydroxyanthraquinone are to be found in the product. The mother liquor and wash waters are transferred to a 100 ml volumetric flask, where the amount of mercury is determined. From the amount of mercury found in the solution, calculated in percent on the weight of sample taken and referred to the maximum amount of mercury present in the original substance – α-anthraquinonylmercury chloride, the degree of hydrolysis of the substance is determined in accord with the scheme:

$$RHgCl + HOH(H_2SO_4) \longrightarrow HgSO_4 + HOH + HCl + RH.$$

SUMMARY

1. The hydrolysis of α-anthraquinonylmercury chloride in different concentrations of sulfuric acid was studied. It was established that the most complete hydrolysis is obtained in 75% sulfuric acid. With increase in sulfuric acid concentration the hydrolysis is retarded and in anhydrous sulfuric acid it hardly proceeds at all.

2. It was established that the hydrolysis of RHgCl is hindered by the addition of mercury sulfate due to the mercuration of anthraquinone, which reaction proceeds concurrently with the hydrolysis reaction.

3. The new mercuric chloride adducts of α-anthraquinonediazonium acid sulfate and nitrate were prepared, which adducts, as well as the α-anthraquinonediazonium chloride-mercuric chloride adduct, are smoothly transformed, using the method of Nesmeyanov, into α-anthraquinonylmercury chloride.

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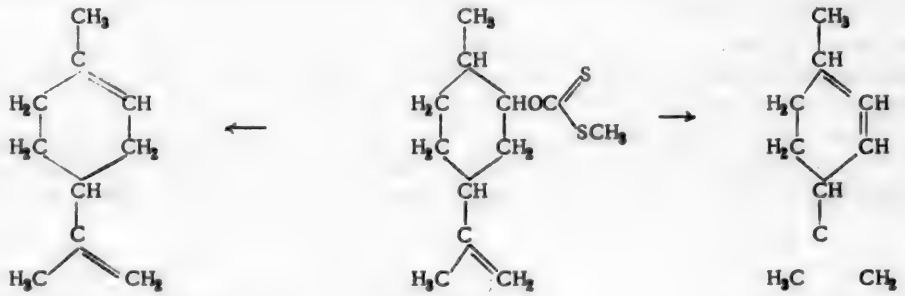
STUDY OF THE HYDROCARBON ISOLIMONENE

G. V. Pigulevsky and I. S. Kozhina

In 1900 L. A. Chugaev [1] obtained in the dehydration of dihydrocarveol via the xanthation method a mixture of two hydrocarbons: limonene (I) and a new terpene, which Chugaev later named isolimonene [2]. The latter differed from limonene in that it had a lower boiling point and a considerably higher specific rotation. In addition, in contrast to limonene, isolimonene failed to give a crystalline tetrabromide or nitrosochloride. In 1907 Chugaev [3] obtained the optical antipode of isolimonene.

Proceeding from the two possible directions for the decomposition of the methyl ester of dihydrocarvylxanthic acid (II),



(I) (II) (III)

Chugaev assigned to isolimonene the structure $\Delta^{1,8(9)}$-p-methadiene (III).

In 1921 Henry and Paget [4], in studying the hydrocarbon fraction of chenopodium oil from Chenopodium ambrosioides var. anthelminticum, found a terpene hydrocarbon, which gave an optically inactive tetrabromide with m.p. 117°. However, the hydrocarbon was not isolated by them: the mixture, serving as the subject of the investigation, failed to contain more than 10-12 % of the hydrocarbon. An investigation of the tetrabromide, and also of the oxidation products of the hydrocarbon fraction of the chenopodium oil, led Henry and Paget to conclude that the hydrocarbon is $\Delta^{1,8(9)}$ -p-menthadiene.

As a result, two hydrocarbons with entirely different chemical properties – the isolimonene of Chugaev and the terpene from chenopodium oil – were assigned the same structural formula of $\Delta^{1,8(9)}$ -p-menthadiene.

It should be mentioned that the isolimonene of Chugaev was later apparently obtained by a number of investigators: Merezhkovsky [5], Doeuvre [6], and Pigulevsky, Kanetskaya and Platonova [8]. However, it failed to represent an individual compound, and its structure had not been proved by anyone;; consequently, it appeared of interest to repeat the synthesis of L. A. Chugaev, isolate the pure isolimonene from the mixture of hydrocarbons, and prove its structure.

We used carvone as the starting material for the synthesis of dihydrocarveol. Dihydrocarveol was converted into the methyl ester of dihydrocarvylxanthic acid, which was then subjected to pyrolysis under the conditions described by Chugaev. The mixture of hydrocarbons obtained in this manner was painstakingly purified in order to remove sulfur compounds.

The separation of limonene and isolimonene was accomplished by repeated fractional distillation. The purity of the obtained isolimonene was controlled by the determination of the specific rotation, preparation of the crystalline tetrabromide, and also by taking the Raman spectra, in which connection the method of taking the Raman spectra proved to be the most effective. The later method was also used by us for proving the structure of isolimonene. The presence in the isolimonene spectrum of a broad line with frequency $\Delta\ \nu$ 1641 cm^{-1} completely agrees with the structural formula of $\Delta^{1,8(9)}$ -p-menthadiene (III) assigned to this hydrocarbon. It is known [9] that the frequency values for a secondary-secondary double bond in a six-membered ring and a primary-tertiary

double bond outside the ring lie in the region 1641-1647 cm^{-1}.

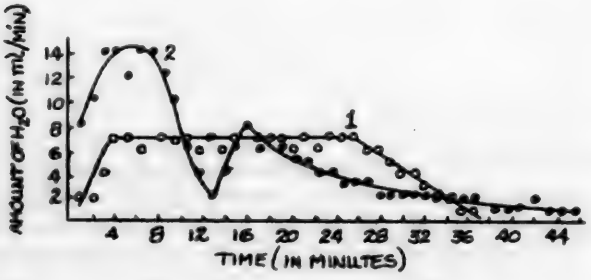
The position of the double bonds in the isolimonene molecule was confirmed by us by the oxidation of isolimonene with potassium permanganate. A liquid keto diacid having the composition $C_9H_{14}O_5$ was isolated, giving a semicarbazone with m.p. 221-222°. The formation of the keto diacid becomes comprehensible if isolimonen is assigned the structure $\Delta^{2,8(9)}$-p-menthadiene.

The treatment of isolimonene with hydrogen bromide and hydrogen chloride gives the corresponding dihydrobromide and dihydrochloride.* The heating of isolimonene hydrochloride with aniline led to the formation of a $C_{10}H_{16}$ hydrocarbon, which, similar to isolimonene, failed to give a crystalline tetrabromide. However, the hydrocarbon was insufficiently pure. It is possible that, in addition to limonene, it also contained $\Delta^{3,8(9)}$ -p-menthadiene as impurity.

The oxidation of isolimonene with benzoyl hydroperoxide according to Prilezhaev [10] gave isolimonene dioxide $C_{10}H_{16}O_2$. For purposes of comparison we prepared the dioxide of the l-limonene obtained by us, together with the dioxide of the isolimonene that was obtained by the decomposition of the methyl ester of dihydro carvylxanthic acid. It was established that the isolimonene is oxidized by benzoyl hydroperoxide at a slower rate than is limonene.

The dioxide of isolimonene was subjected to hydration, which, as it was revealed, proceeded with considerably more difficulty than did the hydration of limonene dioxide. The hydration product of isolimonene dioxide – isolimonene-tetrol – is a glasslike substance having the composition $C_{10}H_{16}(OH)_4$.

An extremely sharp difference in the properties of isolimonene and limonene is observed when they are hydrogenated in the presence of platinum black. Both hydrocarbons form p-menthane in the hydrogenation, but the character of the hydrogenation rate curves is dissimilar. It is known [11, 12] that the double bonds in limonene hydrogenate at a different rate. It was established by us that, in contrast to the hydrogenation curve for limonene, the hydrogenation curve for isolimonene fails to possess an inflexion (see Fig.). Consequently, both of the double bonds in isolimonene are hydrogenated simultaneously; in this connection the hydrogenation rate remains constant.



EXPERIMENTAL

Preparation of the Mixture of Hydrocarbons. The carvone needed for the synthesis of dihydrocarveol was isolated by us from cumin oil. Constants of carvone: b.p. 101-102° at 11 mm, $d_4^{20.5}$ 0.9601, $n_D^{20.5}$ 1.4955, $[\alpha]_D^{20.5}$ +60.9°. Dihydrocarveol was synthesized by the method of Wallach [13]. Its constants were: b.p. 106-107° at 13 mm, d_4^{20} 0.9260, n_D^{20} 1.4793, $[\alpha]_D^{20}$ +30.03°.

The preparation of the methyl ester of dihydrocarvylxanthic acid and its pyrolysis were performed by the method of Chugaev [3]. The mixture of hydrocarbons obtained as the result of the thermal decomposition of the ester was freed from sulfur compounds by steam distillation and subsequent boiling with metallic sodium. Inasmuch as this purification method, recommended by Chugaev, fails to completely free the hydrocarbons of traces of sulfur compounds, we also undertook the shaking of a mixture of the hydrocarbons with an equal weight of metallic mercury for 5 days. After removal of the mercury and filtration, the liquid was distilled in vacuo over metallic sodium. A product with b.p. 69-76° (at 33 mm) was obtained.

Separation of Limonene and Isolimonene. The fractional distillation of the mixture of hydrocarbons through a 0.5 m Vigreaux column permitted the isolation of two main fractions: 1st fraction with b.p. 172-173.5° (at 754 mm) and 2nd fraction with b.p. 175-176° (at 754 mm). The first fraction corresponded to isolimonene, the second to limonene.

Further fractional separation of the hydrocarbons was done in vacuo in a stream of CO_2 through a column with an efficiency of 22.5 theoretical plates. A double distillation of the fraction with b.p. 175-176° gave l-limonene, the constants of which are given in Table 1.

$C_{10}H_{16}$. Found %: C 87.90, 88.06; H 11.96, 11.92.
Calculated %: C 88.15; H 11.88

* See footnote next page.

Repeated distillation through the column of the fraction with b.p. 172-173.5° permitted us to isolate pure isolimonene (see Table 1 for constants).

0.1236 g sub.: 0.3989 g CO_2; 0.1323 g H_2O. 0.1109 g sub.: 0.3574 g CO_2; 0.1195 g H_2O. 1.0034 g sub.: 19.3580 g benzene: Δt 2.01°. 0.8474 g sub.; 15.5448 g benzene: Δt 2.07°. Found %: C 88.01, 87.88; H 11.98, 12.06. M 132.2, 134.9. $C_{10}H_{16}$. Calculated %: C 88.15, H 11.85. M 136.23.

Raman Spectra. The spectra were obtained with the aid of a Zeiss three-prism spectograph. The linear dispersion of the spectrograph close to the excitation line (4358.3 A) was 28 A°/ mm. A GS-2 yellow glass was used as the light filter. The exposure was for 10 hours with an aperture of 0.1 mm.

Spectrum of Isolimonene: 584 (0.5)[1], 695 (1.5), 725 (0.5), 772 (0.5), 827 (0.5), 884 (0.5), 938 (0.5), 964 (0.5), 1014 (0.5), 1072 (1.0), 1102 (1), 1149 (2), 1217 (2), 1282 (3), 1329 (3), 1366 (2), 1390 (3), 1429 – 1454 (4), 1641 (5).

Spectrum of Limonene: 470 (0.5), 495 (0.5), 524 (0.5), 544 (0.5), 639 (0.5), 703 (1), 760 (4), 795 (2), 888 (2), 918 (1), 958 (0.5), 1019 (0.5), 1051 (0.5), 1083 (1.0), 1112 (0.5), 1155 (2), 1206 (1), 1283 (0.5), 1308 (0.5), 1370 (3), 1431 (4), 1457 (4), 1643 (5), 1676 (5).

Attempts to Prepare the Crystalline Tetrabromide and Nitrosochloride of Isolimonene. We used the following methods for the preparation of isolimonene tetrabromide: 1) the action of bromine on a solution of isolimonene in ether-isoamyl alcohol mixture [14], 2) the action of bromine on isolimonene in chloroform solution [4], and 3) the action of gaseous bromine on isolimonene in glacial acetic acid solution [15].

In all cases a viscous bright yellow liquid was obtained, which failed to crystallize either on strong cooling or on prolonged standing (4-6 months) in a vacuum desiccator. Attempts to obtain a crystalline isolimonene nitrosochloride by the action of ethyl nitrite on a solution of isolimonene in glacial acetic acid also failed to give positive results.

Oxidation of Isolimonene. In a round-bottomed flask was placed 4 g of isolimonene and 30 ml of water. With

TABLE

Physical Constants of Isolimonene, Limonene, and Their Dioxides

	Boiling point	d_4^{20}	n_D^{20}	$[\alpha]_D$	$[\alpha]_C$	$[\alpha]_E$	$[\alpha]_F$	$\frac{\alpha_F}{\alpha_C}$	MR_D Found	MR_D Calculated
Isolimonene	56 - 56.5° (at 13 mm)	0.8320	1.4662	– 148.9°	– 113.1°	– 191.5°	– 235.0°	2.08	45.29	45.24
Limonene	63 - 63.5 (at 13 mm)	0.8448	1.4725	– 123.7	–	–	–	–	45.21	45.24
Isolimonene Dioxide	129 - 129.5 (at 31 mm)	1.0237	1.4703	– 37.50	– 29.28	– 47.22	– 58.68	2.00	45.87	45.06
Limonene Dioxide	111 - 113 (at 18 mm)	1.0231 (22°) 1.0287	1.4690	– 55.92	– 44.76	– 55.91	– 68.53	1.97	45.48	45.06

[1] The visual evaluation of the line intensities on a 5-mark scale is given in the parentheses.

* The crystalline dipentene dihydrobromide obtained by L. A. Chugaev in reacting isolimonene with hydrogen bromide can be explained by the heterogeneity of his product, containing about 30 % of limonene as impurity. The amount of limonene contained in Chugaev's isolimonene was determined by us by calculation from the specific rotation values obtained by us for limonene and isolimonene and equating it to the value obtained for Chugaev's isolimonene. This data was confirmed by making a comparison of the line intensities of the double bonds in the Raman spectrum of Chugaev's isolimonene.

constant stirring and cooling of the flask with an ice-salt mixture was added dropwise a 5% aqueous solution of potassium permanganate. On the following day the liquid was filtered from MnO_2, and the precipitate was repeatedly washed with hot water. The filtrate together with wash waters was saturated with CO_2, evaporated in vacuo to a small volume, acidified with sulfuric acid, and repeatedly extracted with ether. The residue after distilling off the ether from the ether solution was a viscous brown liquid (1.5 g). From it was prepared the silver salt.

0.1536 g sub.: 0.0795 g Ag. 0.2006 g sub.: 0.1037 g Ag. Found %: Ag 51.76, 51.70. $C_9H_{12}O_5Ag_2$. Calculated %: Ag 51.92.

The semicarbazone of the keto diacid was also obtained with m.p. 220-221°.

Isolimonene Dihydrochloride. A solution of 16 g of isolimonene in 16 ml of glacial acetic acid was placed in a flask, cooled externally with an ice-salt mixture. HCl gas was passed into the reaction flask for 3 hours. Then the flask contents were poured into cold water. The separated heavy oil was extracted with ether; the ether solution was washed with Na_2CO_3 solution, water, and then dried. After removal of the ether there was obtained a bright yellow oil, which could not be made to crystallize. Yield 20.8 g (84.6%). α_D^{20} −25.0° (c 9.5; alcohol).

0.1735 g sub.: 0.2397 g AgCl. 0.1920 g sub.: 0.2659 g AgCl. Found %: Cl 34.18, 34.21. $C_{10}H_{16} \cdot 2HCl$. Calculated %: Cl 33.92.

Isolimonene Dihydrobromide. In a manner analogous to the previous the dihydrobromide was prepared from 4 g of isolimonene and 25 ml of glacial acetic acid solution saturated in the cold with hydrogen bromide. α_D^{20} −11.6° (c 8.6 : alcohol).

0.1431 g sub.: 0.1816 g AgBr. 0.1397 g sub.: 0.1768 g AgBr. Found %: Br 54.02, 53.82. $C_{10}H_{16} \cdot 2HBr$. Calculated %: Br 53.64.

Cleavage of HCl from isolimonene dihydrochloride [17]. In a round-bottomed flask was placed 16 g of liquid dihydrochloride $C_{10}H_{16} \cdot 2HCl$ and 40 g of freshly distilled aniline. The flask contents were cautiously heated on a sand bath at the boil for 45 minutes. Then the reaction mixture was washed with dilute oxalic acid solution, steam distilled, the distillate shaken with dilute H_2SO_4, thoroughly washed with water, and again steam distilled. This operation was repeated twice. The obtained product was distilled in vacuo over metallic sodium; on doing this there was isolated a fraction with b.p. 50-50.5° (at 10 mm), d_4^{20} 0.837, n_D^{20} 1.4739, $[\alpha]_D^{20}$ 91.1°. Similar to isolimonene, the fraction failed to give a crystalline tetrabromide.

Isolimonene Dioxide. A chloroform solution (375 ml) of benzoyl hydroperoxide (24.88 g), cooled to -8°, was placed in a flask fitted with mechanical stirrer. To the reaction mixture was added dropwise a cold solution of isolimonene in chloroform (9 g of isolimonene in 12 ml of chloroform). The temperature of the reaction mixture was kept at about 4-5°. On the following day the solution was washed with 50% NaOH solution and then water. The residue after distilling off the chloroform was fractionally distilled in vacuo; on doing this a fraction with b.p. 129-129.5° (at 31 mm) was isolated. Yield 8.2 g (see Table for the constants).

0.1602 g sub.: 0.4183 g CO_2; 0.1388 g H_2O. 0.0933 g sub.: 0.2433 g CO_2; 0.0805 g H_2O. Found %: C 71.20, 71.11; H 9.69, 9.65. $C_{10}H_{16}O_2$. Calculated %: C 71.39; H 9.59.

l-Limonene Dioxide. l-Limonene was oxidized in a manner analogous to the oxidation of isolimonene. There was obtained 4.2 g of the dioxide with b.p. 111-113° (at 18 mm) (see Table for the constants).

Hydration of Isolimonene Dioxide. To 2 g of isolimonene dioxide was added 150 ml of water, acidified with 3 drops of concentrated H_2SO_4. The reaction mixture was heated for 4 hours at 45-50°*, after which the formed homogeneous liquid was neutralized with $CaCO_3$, the precipitate filtered, and the filtrate evaporated in vacuo. A viscid colorless substance was obtained, which quickly congealed into a glassy mass. After drying for 6 weeks in a desiccator over $CaCl_2$ the substance was subjected to analysis.

0.1479 g sub.: 0.3172 g CO_2; 0.1323 g H_2O. 0.1102 g sub.: 0.2360 g CO_2; 0.0974 g H_2O. Found %: C 58.49, 58.40; H 10.01, 9.89. $C_{10}H_{16}(OH)_4$. Calculated %: C 58.78; H 9.87.

Isolimonenetetrol is readily soluble in water and ether, less readily soluble in pyridine, and insoluble in ethyl alcohol, xylene and toluene; optically inactive.

* For purposes of comparison we subjected l-limonene dioxide to hydration. The hydration proceeded at room temperature and was accompanied by noticeable heat evolution. Analysis of the obtained product gave the formula $C_{10}H_{16}(OH)_4$.

Catalytic Hydrogenation of Isolimonene. Charge: 0.6066 g of isolimonene, 15 ml of ethyl alcohol, 0.06 g of platinum black. Total amount of absorbed H_2: 210 ml at 20° and 753 mm (calculated 216 ml). Volume of H_2 absorbed each minute (hydrogenation rate): 10,8,10,10,10,9,10,8,10,10,10,10,8,8,10,9,9,9,8,8,7,5,4,4,3,2,1,0,0,0, 1,0,0,0,1 (see Figure).

The hydrogenation product of isolimonene after removal of the alcohol was subjected to distillation, as a result of which was obtained a fraction with b.p. 165-166° (at 757 mm), n_D^{20} 1.4434, α_D^{20} 0°.

Found %: C 85.42, 85.38; H 14.59, 14.72. $C_{10}H_{20}$. Calculated %: C 85.62; H 14.38.

The fraction gave a negative test with bromine water.

Catalytic Hydrogenation of l-Limonene. Charge: 0.6360 g of l-limonene, 15 g of ethyl alcohol, 0.06 g of platinum black. Total amount of absorbed H_2 was 230 ml at 20° and 753 mm (calculated 227 ml). Volume of H_2 absorbed each minute: 16,20,20,20,20,16,12,8,6,2,4,4,4,4,6, 6,6, 6, 6,4,5,5,3,3,3,3,3,2,2,2,2,2,1,1,1,1,1,0,0,1,0,0, 0,0,1,0,0,0 (see Figure).

SUMMARY

1. By the dehydration of dihydrocarveol using the method of L. A. Chugaev was obtained and characterized the purest grade of isolimonene. It was established that the isolimonene obtained by Chugaev contains about 30% of limonene as impurity.

2. The Raman spectrum of isolimonene was taken for the first time, on the basis of which, and also from a study of the products obtained in the oxidation of isolimonene with potassium permanganate, it was shown that isolimonene is $\Delta^{3,8\,(9)}$-p-menthadiene.

3. It was shown that the hydrogenation of the double bonds in isolimonene in the presence of platinum black proceeds simultaneously.

4. The oxidation of isolimonene with benzoyl hydroperoxide gave isolimonene dioxide $C_{10}H_{16}O_2$. Hydration of isolimonene dioxide gives the tetrol $C_{10}H_{16}(OH)_4$.

5. The action of HCl and HBr on isolimonene gave liquid dihydrochloride $C_{10}H_{18}Cl_2$ and dihydrobromide $C_{10}H_{18}Br_2$. The treatment of isolimonene dihydrochloride with aniline led to the formation of impure isolimonene (possibly limonene and $\Delta^{3,8\,(9)}$-p-menthadiene are present as impurities).

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STUDIES OF ACONITE ALKALOIDS

IV. INVESTIGATION OF THE STRUCTURE OF THE ALKALOID ELATINE

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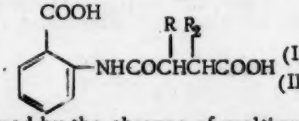
M. S. Rabinovich discovered the alkaloid, elatine $C_{38}H_{50}O_{10}N_2$ in the plant, Delphinium elatum [1]. Saponification of elatine with an alcohol base produced a hitherto unknown alkamine, elatidine ($C_{26}H_{41}O_7N$) and a nitrogenous acid ($C_{12}H_{13}O_5N$), given the name elatinic acid. It has been demonstrated that this is an N-acylated anthranil acid, but that was as far as the study of elatinic acid was carried.

We have discovered, by further study of elatine, that acid hydrolysis of elatinic acid produces not only anthranilic, but also methyl-succinic acid. Thus elatinic acid emerges as one of the isomers of methylsuccinylanthranilic acid (I and II):



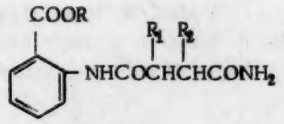
(I) R_1=H, R_2=CH_3
(II) R_1=CH_3, R_2 H,

which is further confirmed by the absence of melting point depression when elatinic acid is mixed with methylsuccinylanthranilic acid obtained by hydrolysis of the alkaloid methyllycaconitine.

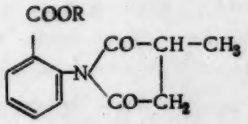
Investigation of the structure of the alkamine elatidine resulted in further confirmation of A. P. Orekhov's hypothesis regarding a structural relationship among the various aconitic alkaloids: a 90% yield of lycoctonine was obtained upon saponification of the methylene dihydroxy group of elatidine under relatively mild conditions by the Clowes-Tollens method [2]. Thus, elatidine differs from lycoctonine by having one methylene dihydroxy group, the place of which is occupied, in the lycoctinine molecule, by two hydroxyls. The structural similarity of lycoctinine and elatidine make clear the unquestionably close relationship between elatidine and the alkaloids methyllycaconitine [3], delsemine [4], avadkharidine [5] and lycaconitine [6], illustrated in the table.

Alkaloids	Hydrolysis Products
Elatine $C_{38}H_{50}O_{10}N_2$	Elatidine, methylsuccinylanthranilic acid
Methyllycaconitine $C_{37}H_{50}O_{10}N_2$	Lycoctinine, methylsuccinylanthranilic acid
Lycaconitine $C_{36}H_{48}O_{10}N_2$	Lycoctinine, succinylanthranilic acid
Delsemine $C_{37}H_{53}O_{10}N_3$	Lycoctinine, methylsuccinylanthranilic acid and ammonia
Avadkharidine $C_{36}H_{51}O_{10}N_3$	Lycoctinine, succinylanthranilic acid and ammonia

The liberation of ammonia in delsemine hydrolysis is to be explained, as demonstrated by Yunusov and Abubakirov, by the fact that one of the carboxyls of methylsuccinylanthranilic acid in the molecule of this alkaloid is bonded in the form of an amide group. The structure of delsemine is expressed by formula (III) (where OR is the remaining lycoctinine). (IV) presents the structure of avadkharidine.



(III) R_1 or R_2 = H; R_2 or R_1 = CH_3
(IV) R_1 = R_2 = H



(V) OR = residual elatidine

Adequate experimental data is lacking as yet to decide how the elatine molecule is built from residual elatidine and methylsuccinylanthranilic acid. It is possible only to advance the hypothesis that the alkaloid is a derivative of an N-substituted imide of methylsuccinic acid (V), bearing in mind that the alkamine elatidine contains only one hydroxyl* group, the molecular weight of the alkaloid**, and its insolubility in bases.

* Found %: OH 3.47. $C_{26}H_{41}O_7N$. Calculated %: OH 3.55.

** 10 mg substance; 93.2 mg camphor; Δt 6.0°; M 715. $C_{38}H_{50}O_{10}N_2$. Calculated: M 694.

Authors note on reading proofs. We demonstrated the presence of the methylsuccinylamide group in elatine and methyllycaconitine by reducing the alkaloids with $LiAlH_4$.

EXPERIMENTAL

Saponification of elatine. 30 g elatine (m.p. 223-225°, but 241-242° in vacuum) was dissolved in 300 ml alcohol, with heating; 15 ml 30% NaOH and 50 ml water were added, and the whole boiled for 30 minutes. The alcohol was distilled off in vacuum until the residue was dry, upon which 500 ml water was added and the precipitated elatidine (17.5 g) filtered off, m.p. 164.5-166.5° (in vacuum 180.5-181.5°). Ether extraction of the mother liquor gave another 2.4 g elatidine, m.p. 168.5-171.5°. After removal of the elatidine, the aqueous mother liquor was acidified by 10% H_2SO_4 and put through ether extraction. Upon distillation of the ether, 10.3 g crystalline elatinic acid was obtained, which melted at 159-160° after crystallization from water; no depression was observed when this acid was mixed with methylsuccinylanthranilic acid obtained by methyllycaconitine hydrolysis.

Saponification of elatinic acid. 3 g elatinic acid was dissolved in 50 ml hot 10% HCl and boiled 1.5 hours. The solution was condensed in vacuum until dry. The residue was dissolved in water, the solution neutralized by caustic soda until it gave a weakly acid reaction to methyl orange, upon which 1.5 g crystalline acid was precipitated (A). The mother liquor was acidified with hydrochloric acid until a strongly acid reaction was obtained with Congo paper, and it was evaporated in a dish till dry. The residue was subjected to fourfold extraction with 75 ml boiling benzene. The amalgamated aqueous extracts were washed with benzene and evaporated till dry. The residue was subjected to fourfold extraction with 75 ml boiling benzene. The amalgamated aqueous extracts were washed with benzene and evaporated till dry. The residue was 1.3 g crystalline acid (B). After crystallization from water, acid A melted at 147-149° and gave no depression when mixed with anthranilic acid. Acid B was recrystallized from acidified water, dried and vacuum distilled at 100° and 0.04-0.06 mm, after which it melted at 114-115°.

	Found %:	C 44.67, 45.58; H 6.00, 5.96
$C_9H_8O_4$.	Calculated %:	C 45.4 H 6.06

A sample mixed with methylsuccinic acid gave no depression.

Saponification of the methylenedioxy group by elatidine. 10 g elatidine was dissolved in 100 ml HCl (1:1) 5 g phloroglucinol in 400 ml HCl (1:1) was added to the solution, and the total heated 2 hours at 70-80°. Depositing of an orange precipitate was observed in the first minutes after this temperature was attained. After heating was ended, the solution was allowed to stand overnight and a phloroglucide was filtered off, which after careful washing on the filter and drying at 105° weighed 3.8 g, indicating that it contained one methylenedihydroxy group (found %: CH_2 3.9, calculated 3.0). After separation of the phloroglucide (without wash water) the filtrate was vacuum condensed to dryness, the residue dissolved in water and alkalized with concentrated aqueous ammonia; the precipitated crystalline base was washed with water on the filter and dried at 60°. The yield was 9 g. Crystallization from 70% alcohol gave elongated needles, m. p. 151.5-153.5° (in vacuum).

0.0622 g sub. 3.05 ml absolute alcohol, l = 0.5 dm., α_D + 0.52° $[\alpha]_D$ + 51.0°.

The hydrochloride was obtained in the usual manner and recrystallized from a mixture of alcohol and ether; upon drying at 100° and 10 mm it had an m.p. of 161-162°

0.0671 g sub. 3 ml water; l = 0.5 dm., α_D + 0.16°, $[\alpha]_D$ + 14.2°.

	Found %:	C 57.55, 57.61; H 8.37, 8.57; Cl 7.28, H_2O 2.2
$C_{25}H_{41}O_7N \cdot HCl \cdot 2/3\,H_2O$.	Calculated %:	C 58.1; H 8.26; Cl 6.89, H_2O 2.3

This base gave no depression of melting point upon mixing with the base, lycoctinine.

SUMMARY

The structure of hydrolysis products of the alkaloid elatine, was studied. It was shown that elatinic acid is one of the isomers of methylsuccinylanthranilic acid. The alkamine elatidine resembdes lycoctonine, differing from the latter by the presence of a methylene dihydroxy group instead of the two hydroxyl groups.

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